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THE ENTHALPY OF FORMATION OF ZINC PHOSPHIDE Zn_3P_2

S. A. Shchukarev, G. Grossman and M. P. Morozova

Zinc and phosphorus, as was shown by Stackelberg [1], form two compounds Zn_3P_2 and ZnP_2. The phosphide, Zn_3P_2, which is formed by the action of phosphorus vapors on metallic zinc, has been studied to the greater extent. We used vacuum-distilled zinc, and red phosphorus which had been freed from oxide and acid impurities by washing with water, and which had been dried to constant weight over phosphoric anhydride. Zinc and phosphorus (taken in considerable excess) were placed in different combustion boats in a glass tube, which was carefully evacuated to a high vacuum, and was later unsoldered. The tube was placed in a long tube furnace and heated along its entire length at about 400-450°. After two days, the tube was partially drawn from the furnace and, in order to remove the excess phosphorus, was heated only at the part where the zinc phosphide combustion boat was. The preparation obtained in this way, according to analytical data, had a composition which for all practical purposes corresponded to the formula Zn_3P_2, and its X-ray photograph agreed with that obtained for Zn_3P_2 by Stackelberg.

Zinc phosphide reacts very slowly with acid; therefore, for calorimetric purposes we had to employ the reaction of its combustion in oxygen, which leads, as was shown by chemical analytical data and by X-ray data, to the formation of zinc orthophosphate. In order to assure complete combustion of the phosphide, a certain accurately measured quantity of benzoic acid was added to it, and the resulting mixture was pressed into tablets. The latter were placed in a small weighed collodion bag; the reaction was initiated by ignition of a small spiral of fine platinum wire. The combustion was carried out in an ordinary type of calorimetric bomb at an oxygen pressure of 25 kg/cm². The bomb was suspended inside of the calorimetric jacket, which was placed in a large (100 liters) water thermostat, the temperature of which was maintained at 25 ± 0.005°. In the cover of the calorimetric bomb there was a recess, in which a thermal resistance of the MMT-1 type was placed. In order to assure thermal contact of the thermal resistance with the bomb, the entire free volume of the recess was filled with copper filings. The resistance of the "thermistor" was measured with a Wheatstone bridge with an accuracy of about 0.1Ω, which corresponded to 0.0002°.

The thermal capacity of the calorimeter was determined with benzoic acid.

For the enthalpy of combustion of zinc phosphide, −583 ± 3 kcal/mole (with calculation of all necessary corrections) was found.

$$Zn_3P_{2\,solid} + 4O_{2\,gas} = Zn_3(PO_4)_{2\,solid} + 583 \text{ kcal.}$$

The enthalpy of formation of zinc phosphate was not known; therefore, we determined the enthalpy of solution of the Zn_3P_2 combustion product in dilute (0.3 N) sulfuric acid.

In preliminary experiments, it was found that, because of its small value, the enthalpy of mixing of the zinc sulfate and orthophosphoric acid solutions (taken in the concentrations used in the determination of the heat of solution of the Zn_3P_2 combustion product) can be neglected. The enthalpy of solution was found to equal −48.6 kcal/mole.

$$Zn_3(PO_4)_{2\,solid} + 3H_2SO_{4\,aq.} = 3ZnSO_{4\,aq.} + 2H_3PO_{4\,aq.} + 48.6 \text{ kcal.}$$

Hence, the enthalpy of formation of the zinc orthophosphate obtained was equal to −684 kcal/mole:

$$3Zn_{solid} + 2P_{solid} + 4O_{2\,gas} = Zn_3(PO_4)_{2\,solid} + 684 \text{ kcal.}$$

On the basis of this value and the value of the above-specified enthalpy of combustion of zinc phosphide, the enthalpy of formation of the latter was −98 ± 3 kcal/mole:

$$3Zn_{solid} + 2P_{solid} = Zn_3P_{2\,solid} + 98 \pm 3 \text{ kcal.}$$

The enthalpies of formation of the nitride (Zn_3N_2) [2] and of the arsenide (Zn_3As_2) [3] are known; the latter, apparently, are not particularly accurate. They are equal to −3.5 kcal/mole and −29 kcal/mole, respectively.

Thus, as in the case of the magnesium compounds of the elements of the main subgroup of Group V [4], the course of the enthalpies of formation of the zinc compounds obeys the law of secondary periodicity [5]. On going from the nitride to the phosphide, we observe an increase of the enthalpy of formation, but the transition from the phosphide to the arsenide, on the other hand, is accompanied by a decrease of the enthalpy of formation.

SUMMARY

1. The enthalpy of formation of zinc phosphide Zn_3P_2 was found to equal -98 ± 3 kcal/mole.

2. The course of the enthalpies of formation of zinc compounds with nitrogen, phosphorus, and arsenic obeys the law of secondary periodicity.

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INVESTIGATION OF METALLIC NITRIDES

II. THE SUBNITRIDES OF STRONTIUM AND BARIUM

S. M. Ariya, E. A. Prokofyeva and I. I. Matveeva

In 1951 we synthesized the higher nitride of barium, the pernitride, BaN_2 [1], the possibility of the synthesis of which, under the conditions of thermodynamic equilibrium with its decomposition products, was predicted by S. A. Shchukarev's [2] isoatom method.

For the same system, Ba–N, the isoatom method also leads to the prediction of the possibility of synthesis of barium subnitride, Ba_2N (also under the conditions of thermodynamic equilibrium with decomposition products).* In the same way, the isoatom method gave bases for expecting the existence of a stable strontium subnitride Sr_2N. The problem of alkaline earth metal compounds, in which anomalously low formal valences would appear, was discussed in the literature very long ago.

From the time of the work of Güntz [3] until recently, the existence of subhalides, for example SrCl, BaBr, BaI, etc., was recognized. Even the enthalpies of formation of preparations of gross-composition, which corresponded to these formulas, were determined.

In 1949 Cubicciotti and Thurmond [4] showed that in the systems, $SrCl_2$–Sr, $BaBr_2$–Ba, etc., a marked mutual solubility of the phases in the liquid state and a negligible mutual solubility in the crystalline state occurs.

These authors observed no compounds of a composition found in the intermediate $MeHal_2$–Me. The alkaline earth metals formed no compounds with oxygen in which their formal valence would be less than two.** In 1953 Libewitz [5] found that barium oxide, existing in equilibrium with metallic barium, contained an excess of barium by 0.085-0.14%, which he accounted for either by the presence of barium atoms in the interstices, or the presence of vacant positions in the oxygen lattice of BaO. Thus, sub-compounds did not exist in the Ba–O system. S. A. Shchukarev [2] showed that, if we consider the binary combinations of any definite element with a series of different elements, then there should be more thermodyamically stable forms of the combinations by this second element, the lower its enthalpy of atomization (i.e., the enthalpy of the process of conversion of a gram-atom of the element to the monatomic gas state).

From this point of view, thermodynamically stable sub-compounds of the alkaline earth metals are most probable with nitrogen, since compared to nitrogen, their enthalpies of atomization are the lowest (enthalpy of atomization of nitrogen 112.5 kcal, oxygen 59.2 kcal., halogens 29-20 kcal).

In accordance with this consideration, we undertook the investigation of the decomposition of barium and strontium nitrides (Sr_3N_2 and Ba_3N_2) in vacuo. This investigation showed that strontium and barium nitrides at 450-500° C, and at a pressure of the order of 10^{-3} mm lose nitrogen, with the formation of products of the compositions Sr_2N and Ba_2N. This decomposition is completed rather quickly (in the course of 1-2 hours). Further heating for as long as desired (to several days) led to no further separation of nitrogen. It was impossible that this partial expulsion of nitrogen was connected with the process:

$$Ba_3N_{2\,solid} \longrightarrow 3Ba_{solid} + N_{2\,gas}. \qquad (1)$$

* We recall that the isoatom method consists of the fact that, if we plot the composition of the compounds of two elements on the horizontal axis, and their enthalpies of formation from free atoms on the ordinate, referred to 1 g-atom of the compound or of the corresponding element $\frac{\Delta H_i}{n}$, then the points obtained would connect with each other, forming a smooth curve, and offering the possibility of interpolation, and sometimes also of extrapolation, of unknown enthalpies of formation.

** Later, as this article went to press, a work of G. Wehner appeared [G. Wehner, Z. allg. anorg. Chem., 276, 72 (1954)], in which he reported on the production, by means of chilling melts of the composition CaCl, of an individual compound of this formula.

since it is accompanied by the absorption of 89.9 kcal, and even the large entropy increase (probably of the order of 40 entropy units) does not render its operation at 500° C feasible.

The equilibrium pressure of nitrogen, which corresponds to process (1) at 500° C, would probably consist of a value of the order of 10^{-9}-10^{-7} mm, whereas in our experiments, the decomposition of the nitrides took place at a pressure no smaller than 10^{-3}-10^{-2} mm.

Moreover, in the case where process (1) would be possible under these conditions, it would probably go to completion; in any case the decomposition of Me_3N would not correspond to the end of decomposition. The composition of the products which formed was always very close to that which corresponds to the formula Ba_2N.

The reaction of the subnitrides with water is effected in accordance with the equation:

$$Me_2N + 4H_2O = 2Me(OH)_2 + NH_3 + \tfrac{1}{2} H_2.$$

The ratio of the total quantity of hydrogen (free and entering into the composition of ammonia) to the quantity of nitrogen (these quantities being expressed in gram-atoms) which formed during hydrolysis, for pure subnitrides of the formula Me_2N, probably equals four. The preparations obtained in our experiments gave the following values of this ratio:

decomposition product of Sr_3N_2 in vacuo 4.12, 3.94;

decomposition product of Ba_3N_2 in vacuo 4.06, 4.12, 3.97.

These data show that in both cases, under the conditions described, there is no basis for doubting the formation of subnitrides of the formula Me_2N, which may also be represented as $Me_3N_2 \cdot Me$. An X-ray investigation showed that the conversion of Sr_3N_2 to Sr_2N was accompanied by a change of crystalline structure. The subnitrides do not differ in external form from the original nitrides – they are black, finely crystalline powders.

The specific electrical conductivity of Ba_2N was found to be of the order of $10^{-2}\Omega^{-1}$ at room temperature.* The temperature coefficient of the electrical conductivity was negative. In other words, we can assume the presence in this compound of metallic, electronic conductivity.

The electrical conductivity of typically metallic nitrides of the TiN, VN, etc., type is considerably higher, by several orders; however, for Ba_2N we have some approximation of the properties to those for the metallic phases. By the isoatom method, the enthalpy of formation of barium subnitride was estimated at 51 kcal/mole.

This value was found experimentally by a determination of the difference of the enthalpies of solution of barium nitride and barium subnitride, obtained by the decomposition of the same barium nitride preparation, for which the enthalpy of solution in hydrochloric acid had been determined.

This excluded the effect of impurities on the value sought, inevitable in preparations of such active substances as the alkaline earth nitrides and subnitrides.

The reaction of barium nitride with hydrochloric acid proceeds according to the equation

$$Ba_3N_2 + 7.297HCl = 3BaCl_2 + 1.297NH_4Cl + 0.349N_2 + 0.1047H_2 \qquad (2)$$

For the subnitride:

$$3/2Ba_2N + 7.325HCl = 3BaCl_2 + 1.325\ NH_4Cl + 0.067N_2 + 0.963H_2. \qquad (3)$$

The difference of the enthalpies of solution of the nitride and subnitride containing the same amount of impurities, by calculation of the values of the enthalpies of formation and enthalpies of solution of ammonium chloride (by calculation of different values of the coefficients of ammonium chloride beforehand by the formula in Equations 2 and 3), calculated for 1 mole of Ba_3N_2, obviously gives the enthalpy of the process:

$$Ba_3N_2 = \tfrac{3}{2}Ba_2N + 0.25N_2. \qquad (4)$$

This value was found equal to 8.8 kcal. With the calculation of the enthalpy of formation of Ba_3N_2 equal to −89.9 kcal/mole [6], this gives -53.4 ± 2 kcal/mole (at 25° C and a pressure of 1 atm) for the enthalpy of formation of Ba_2N.

$$2Ba_{solid} + \tfrac{1}{2}N_{2\,gas} = Ba_2N_{solid} + 53.4 \pm 2 \text{ kcal}.$$

* The electrical conductivity of the nitride corresponding to the ordinary valences of barium and nitrogen was lower by many orders.

The value obtained is close to that predicted by S. A. Shchukarev's isoatom method, which emphasizes once more that this method is one of the most important generalizations of the thermo-chemistry of binary compounds.

The chemical structure of the subnitrides requires, of course, still further study. For the present it may be assumed that in these compounds part of the valence electrons of the barium atoms provide a bond similar to a metallic bond.

It is not very likely that in the subnitride lattices there are Ba^{+} ions (i.e., $Ba^{++}Ba^{+}N^{\equiv}$), since a phase of such a structure would have a very low lattice energy, insufficient for compensation of the large endothermic effect of the process of addition of three electrons to a nitrogen atom, the endothermic effect of the dissociation of a nitrogen molecule to atoms, etc.. For just this reason, because of the low lattice energy values (due to the small charge values of the cations), the nitrides of sodium and the heavier alkali metals are unstable.

Thus, one can hardly assume that in the subnitrides we are actually dealing with the reduced valence of strontium and barium: both of these elements, of course, are bivalent, but some of their valence bonds are utilized in metallic type bonds. It should again be noted that it is impossible to calculate the enthalpy of formation of such compounds on the basis of ideas concerning chemical bonds.

How do you account for such a smooth slope of the isoatom, which offers the possibility of estimation of the enthalpy of formation values of compounds, the structure of which we do not know? As one of the reasons for this, we should point out the fact not considered by contemporary quantitative lattice theories, that in the crystalline phases, "bond" interaction also occurs between atoms of the same element (probably contributing an appreciable share to the enthalpy of formation value of the compounds).

This circumstance was definitely indicated by a number of physical properties, as is known by the magnetic properties of many compounds of elements of subsidiary sub-groups, the magnetic susceptibilities of which, as a rule, are smaller by calculation on the assumption of the presence in their lattices of free ions of these elements, which react with each other only electrostatically. These reduced values of the magnetic susceptibility are usually interpreted as the result of the existence of ordinary type atomic bonds between cations of the elements of subsidiary sub-groups (Klemm [7]).

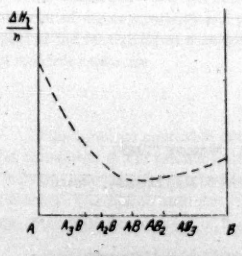

Fig. 1. Typical form of isoatom.

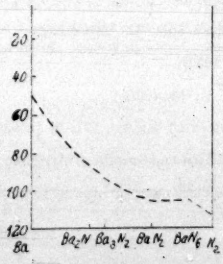

Fig. 2. Isoatom of the Ba—N system based on assumption of an enthalpy of dissociation of molecular nitrogen, equal to 225.1 kcal/mole.

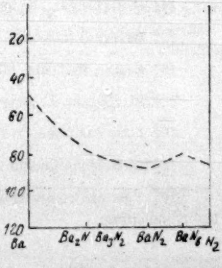

Fig. 3. Isoatom of the Ba—N system on basis of assumption of an enthalpy of dissociation of molecular nitrogen, equal to 170.2 kcal/mole.

In a number of cases, even in compounds of the type of the salts of oxygen acids, the metal atom has an adjacent metal atom at a distance very small in contrast to the interatomic distances in the lattice of the given metal. This, for example, occurs in the case of copper acetate [8]. It is natural that a larger number of such bonds between the atoms of the same elements will be present, the higher the relative content of the given element in the compound. The fact that the ordinate points of the compounds rich in any element, are close to the ordinate corresponding to the characteristic element is also explained by this fact.

The bonds between atoms of different elements, as indicated by S. A. Shchukarev [2], are more stable than the bonds between atoms of the same element. Such bond contributions will be greatest in compounds in which both elements are present in equal quantities, i.e., in compounds of the AB form. Actually, an isoatom minimum often occurs either for this form or for one close to it.

Thus, an isoatom of the most typical form is cited in Fig. 1. The data that we obtained on the enthalpy of formation values of Ba_2N and BaN_2 enabled us to construct an isoatom for the Ba–N system.

It is necessary to point out that the enthalpy of formation value of molecular nitrogen from the free atoms, determined spectroscopically, until recently was questionable (which was connected with the difficulties of interpretation of the spectrum of the N_2 molecule).

In Fig. 2, the isoatom for the Ba–N system is presented, on the basis of the assumption that the enthalpy of dissociation of molecular nitrogen was equal to 225.1 kcal/mole [9]; in Fig. 3 the same isoatom is represented on the basis of an enthalpy of dissociation of molecular nitrogen, equal to 170.2 kcal/mole [10] (older value, however, the most prevalent at the present time).

Figs. 2 and 3 show that both isoatoms have the usual shape, which is also clear; since the enthalpy of atomization of nitrogen figures in all points of the isoatoms, therefore, a certain change in it cannot alter the form of the curve.

SUMMARY

1. The existence of alkaline earth metal subnitrides of the formulas Sr_2N and Ba_2N, representing compounds of the metallic type, was established. The feasibility of production of these compounds, under conditions of thermodynamic equilibrium with their decomposition products, was predicted by S. A. Shchukarev's isoatom method.

2. The enthalpy of formation of Ba_2N, determined calorimetrically, was found to equal -53.4 ± 2 kcal/mole.

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COMPOSITION AND PROPERTIES OF A HYDROCHLORIC ACID SOLUTION OF NIOBIUM PENTOXIDE

S. I. Solovyev, E. I. Krylov and V. F. Degtyarev

According to literature data [1], freshly precipitated niobic acid does not react visibly on boiling with concentrated hydrochloric acid. The precipitate peptizes on subsequent dilution with water, with the formation of a clear sol of niobic acid. In this way, Weinland and Storz [2] obtained a 7% colloidal solution of niobic acid. Unlike a β-stannic acid sol, niobic acid did not coagulate on gradual introduction into a cold solution of fuming hydrochloric acid, but formed niobium oxychloride, the solution of which was entirely clear, and which could contain about 0.8% $NbOCl_3$.

Vik. Spitsyn and N. A. Preobrazhensky [3] showed that at high temperatures niobium oxychloride is hydrolyzed by water vapor. In the hydrolysis products at temperatures above 300° they found black niobium oxychloride, the composition of which corresponded to the formula NbO_2Cl, but at lower temperatures a white sublimate formed. This white sublimate contained: Nb_2O_5 67%, HCl 14%, H_2O 14% and $NbOCl_3$ 5%. It consisted of colloidally-dispersed niobium pentoxide, which adsorbed hydrogen chloride and water vapor. The amount of hydrogen chloride adsorbed depends on the degree of hydration of the colloidal niobium pentoxide; the more hydrated the niobium pentoxide, the more hydrogen chloride is adsorbed. Thus, opinions concerning the nature of the binding of hydrogen chloride by freshly precipitated niobic acid are contradictory; according to a certain datum [2], the chemical interaction of niobic acid with concentrated hydrochloric acid proceeds according to the equation:

$$H_3NbO_4 + 3HCl \rightleftharpoons NbOCl_3 + 3H_2O,$$

but according to another [3], adsorption of the hydrogen chloride by the hydrated colloidally-dispersed niobium pentoxide occurs.

Unlike many other niobium compounds, the compound being considered is stable toward slightly acid solutions at room temperature, and should, therefore, be of definite practical interest. The purpose of this work was the establishment of the composition and properties of a hydrochloric acid solution of niobium pentoxide, and the establishment of the feasibility of extending the views of Vik. Spitsyn and N. A. Preobrazhensky concerning colloidal solutions of niobium pentoxide.

EXPERIMENTAL

Pure niobium pentoxide containing 99.5% Nb_2O_5, 0.38% TiO_2 and 0.14% Ta_2O_5 served as the starting material. For conversion to the soluble state, the niobium pentoxide was fused with potassium pyrosulfate. On cooling, the finely ground melt was leached with concentrated sulfuric acid. Niobic acid was precipitated from this solution by ammonia. The niobic acid precipitate was washed several times by decantation with hot water, and was washed on the filter until the removal of traces of sulfate ions.

A weighed portion of about 20 g of the freshly precipitated niobic acid was treated in a conical flask by stirring with a glass rod with 50 ml of concentrated hydrochloric acid, at first in the cold, but later on boiling. The suspension obtained, still in the hot form, was quickly separated from the excess hydrochloric acid by filtration through a No. 4 glass filter. On the filter the precipitate instantly dissolved in 150-200 ml of distilled water. The filtered solution became completely clear, and only on storage for several days did it acquire a noticeable opalescence, but without separation of a precipitate. In further statements we will call this the chloride solution.

Methods of chemical analysis. The niobium pentoxide content in the chloride solution was determined by two gravimetric methods of analysis: by precipitation with ammonia and by hydrolysis of a dilute solution by heating. On dilution of 2 ml of the chloride solution to 50 ml with water, and boiling for 1-2 minutes, hydrolysis proceeded immediately: all of the niobic acid precipitated completely. The precipitate could be collected quantitatively on a filter, since the niobic acid liberated from the hydrochloric acid by the hot hydrolysis dissolved neither in cold nor in hot water.

TABLE 1

Chemical Analysis of Chloride Solutions of Niobium Pentoxide

Chloride solution	Content of ions (mg/ml)		Ratio by wt.
	niobium	total chlorine	Nb:Cl
1	5.89±0.02	24.26	1:4.12
2	1.61±0.03	5.69	1:3.53

The total hydrochloric acid content in the chloride solution was determined acidimetrically and was verified by titration with silver nitrate. An aliquot of the solution, neutralized by alkali to the equivalence point, was filtered off from the depositing precipitate of niobic acid, and the chloride ion content in the filtrate was determined by a direct titration with 0.1 N $AgNO_3$. The results of the determination of chloride-ions by silver in all cases agreed exactly with the acidimetric determinations. All the work was completed with two chloride solutions (Table 1).

The ratio by weight of niobium to chlorine did not remain constant, but varied with the conditions of preparation of the chloride solution. In connection with this, a necessity developed for a more thorough determination of the character of the acidity of the solution by the conductometric method of analysis.

Results of the conductometric analysis. Conductometric titrations were carried out with solutions of alkali, sodium and potassium oxalate, potassium and sodium fluoride and some other salts, whereby it was found that one portion of the acidity titrated as free acid, and another as acid combined with niobium, and occurring with it in a constant ratio (Table 2).

TABLE 2

Conductometric Titration of Chloride Solutions of Niobium Pentoxide in Various Solvents

Solution for titration and its normality	Quantity of niobium (mg/ml)		Quantity of hydrochloric acid (mg/ml)		Molar ratio $Nb:HCl_{combined}$
	conducto-metric	gravimetric	free	combined	
NaOH (1.02711)	1.54	1.61±0.03	4.00	1.85	1:3
$KNaF_2$ (0.6)	1.608	1.61±0.03	4.70	1.88	1:3
$K_2C_2O_4$ (0.8876)	6.13	5.89±0.02	17.9±0.14	7.03±0.14	1:3

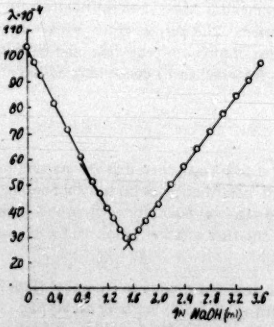

Fig. 1. Conductometric titration of chloride solution of niobium with a solution of alkali.

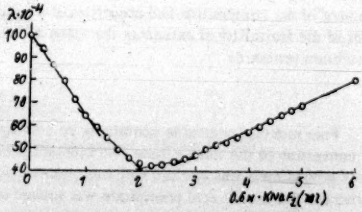

Fig. 2. Conductometric titration of the chloride solution by a potassium-sodium fluoride solution.

a) Conductometric titration with a solution of alkali. 10 ml of the second chloride solution of niobium, diluted to 100 ml with water, was back-titrated with 1.56 ml of 1.02711 N NaOH. On the titration curve (Fig. 1) there is a discontinuity corresponding to the boundary of the titrations of free and combined hydrochloric acid, and corresponding to 1.08 ml of alkali solution, or 0.494 ml of combined hydrochloric acid.

According to data from the gravimetric analysis, in 10 ml of the solution analyzed there was 0.168 mg-atom of niobium. Consequently, the quantity of combined hydrochloric acid corresponded to a constant proportion: 0.494:0.169 = 3:1, i.e., to three molecules of HCl per atom of niobium. From this the equivalent ratio of niobium per 1 ml of a N solution of alkali will equal 31.17 mg. Hence, the niobium content in 10 ml of solution corresponds

to 15.4 mg, which within the limits of experimental error, agrees with the gravimetric determination (Table 1), since the graph may be read with an accuracy of about 1 mm, which corresponds to 0.6 mg of niobium.

b) Conductometric titration with a solution of potassium-sodium fluoride. 10 ml of the second chloride solution of niobium was back-titrated with a 0.6 N solution of $KNaF_2$. There are clearly three discontinuities on the titration curve (Fig. 2).

The niobium content in 10 ml of solution was equal to $0.86 \cdot 0.6 \cdot 31.17 = 16.08$ mg, which agreed with the gravimetric determination.

c) Conductometric titration with a solution of potassium oxalate. It is known that niobic acid forms complexes with oxalic acid [2]. It was of practical interest to investigate the formation of oxalate complexes between the chloride solution of niobium studied and potassium oxalate. The results of titration of 2 ml of the first chloride solution of niobium are presented in Fig. 3. On the graph there is a distinctly expressed discontinuity. A conductometric titration by potassium oxalate enabled us to show that, at first the excess of free hydrochloric acid was removed, then there was a replacement of the hydrochloric acid combined with niobium by oxalic acid, which forms a complex compound with niobic acid.

According to analytical data, the number of gram-atoms of niobium in a unit of volume, was equal to 6.13 mg/ml, which agreed satisfactorily with the gravimetric determination.

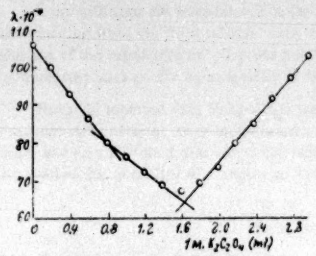

Fig. 3. Conductometric titration of a solution of niobium by a solution of potassium oxalate.

The results of the conductometric titration are recorded in Table 2.

The data cited confirmed the constant ratio between niobium and combined hydrochloric acid as equal to 1:3. The quantity of free hydrochloric acid varied with the conditions of preparation of the chloride solution of niobium pentoxide.

Weinland and Storz [2] assumed that niobic acid, on treatment with hydrochloric acid, forms niobic oxychloride $NbOCl_3$. The chloride solution of niobium which we obtained actually contained, in the combined state, three molecules of hydrochloric acid (or three chloride ions) per atom of niobium, and somewhat of an excess of free hydrochloric acid, as was demonstrated by conductometric titrations with alkali, oxalate and other salts. Hydrated niobic oxychloride was the basis of the chloride solution.

The nature of the relation between niobic acid and hydrochloric acid in aqueous solutions was different from that assumed by Vik. I. Spitsyn and N. A. Preobrazhensky for solid, colloidally-dispersed niobium pentoxide.

SUMMARY

The freshly precipitated hydrate of niobium pentoxide, on treatment with concentrated hydrochloric acid and brief heating at the boiling point, gave a water-soluble chloride compound, the properties and composition of which were studied by the method of conductometric titration.

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THE HYDRATABILITY AND SOLUBILITY OF MANGANOUS FLUORIDE

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As is known, similar compounds of neighboring transition metals usually show marked similarity as to crystalline form, capacity for formation of crystal hydrates, composition of crystal hydrates, solubility, etc.

The anhydrous difluorides of metals of the middle of the fourth period of the D. I. Mendeleev system, from manganese to nickel and zinc fluoride, crystallize according to the rutile type; the parameters of their unit cells and their metal-fluorine interatomic distances vary smoothly:

	MnF_2	FeF_2	CoF_2	NiF_2	CuF_2	ZnF_2
Interatomic distance Me—F in A	2.11	2.12	2.09	2.06	2.34	2.10

It is interesting that in the Mn—F interatomic distance no abnormally high value of the Mn^{++} radius appeared, as found by Goldschmidt from the interatomic distances of oxides; the sum of the ionic radii of F^- and Mn^{++} is much smaller according to Goldschmidt. Out of this series, cuprous fluoride precipitates, crystallizing in the fluorite lattice. The structure of CrF_2 crystals has remained unstudied.

Contradictions are encountered in the literature data on the composition of the crystal hydrates of these fluorides. Judging from the most reliable data, the fluorides of bivalent iron, cobalt, nickel and zinc precipitate from solutions as the tetrahydrates. Cuprous fluoride also precipitates from this series — its hydrate has been described. Contradictory data on the hydratability of manganous fluoride are well-known.

Nuka [1] reported that $MnF_2 \cdot 4H_2O$ precipitates on evaporation of a saturated solution of manganous fluoride in a vacuum-desiccator at room temperature. Biltz and Rahlfs [2] obtained this salt by the same method. Kurtenacker, Finger and Hey [3] found that anhydrous MnF_2 formed on dissolving $MnCO_3$ in concentrated hydrofluoric acid. They also studied the solubility of manganous fluoride in hydrofluoric acid at 20°:

HF (%)	5.28	17.05	36.42
MnF_2 (%)	2.88	3.73	0.72

Using the residue method of Shreinemakers, they showed that in all cases anhydrous MnF_2 was the bottom phase. Therefore, they assumed that $MnF_2 \cdot 4H_2O$ also did not exist as a stable phase.

According to Nuka's data [1], $MnF_2 \cdot 4H_2O$ effloresces in the air at room temperature (after a month the salt contained 0.3 mole of water); at 50° almost all the water was removed, but the rest of it was removed only at above 100°, with simultaneous partial hydrolysis and oxidation of the salt. For the solubility of the crystal hydrate (expressed in percentages of the anhydrous salt) Nuka cited the following values:

Temperature	20°	40°	60°	100°
MnF_2 (%)	1.05	0.66	0.44	1.48

It should be pointed out that Nuka did not determine the composition of the bottom phases. A decrease of the solubility of the highly hydrated salt with an increase of the temperature does not appear likely, since similar salts usually dissolve endothermically; it can be assumed that Nuka's data (at least for 40° and higher temperatures) refers to the anhydrous salt.

The investigation of the possibility of the stable existence of $MnF_2 \cdot 4H_2O$, and investigation of the conditions of its conversion to the anhydrous form were the objects of the present work. As we demonstrated, the tetrahydrate is stable below 23.5°.

EXPERIMENTAL

1. Direct synthesis of MnF_2 and $MnF_2 \cdot 4H_2O$. On dissolving manganous carbonate in 40% hydrofluoric acid, a large evolution of heat from the pulp resulted (about 30-40°, at an ambient temperature of 20-25°); as shown by a microscopic investigation and a determination of the composition of the bottom phase by the residue method, perhaps anhydrous MnF_2 with a small admixture of tetrahydrate forms directly at the same time (in the residue several per

cent of water was detected). In the residue, 1.7-2.3% of H_2O was determined by rapidly washing with alcohol and ether, and drying in the air at 120°.

If manganous carbonate is dissolved in dilute hydrofluoric acid cooled to 0°, as was demonstrated by the use of the residue method, $MnF_2 \cdot 4H_2O$ is included in the bottom phase (Table 1, Fig. 1).

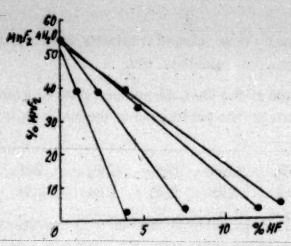

Fig. 1. Composition of solutions and bottom phase at 0°.

TABLE 1

Compositions of Solutions and Moist Bottom Phase at 0°

Expt. No.	Solution composition (in %)		Residue composition (in %)	
	HF	MnF_2	HF	MnF_2
1	3.85	2.80	1.05	38.75
2	7.56	3.65	2.31	38.54
3	12.00	3.53	4.78	33.72
4	13.28	5.10	3.66	39.43

The manganese content in the solution and in the residues was determined by the bismuthate method. Since the presence of F^- ions interferes with this determination [4], boric acid was introduced in order to bind the F^- in solution; moreover, entirely satisfactory results were obtained:

Mn taken (in mg): 39.65, 34.72. Found Mn (in mg): 39.57, 34.69.

The total fluorine content in the solutions and in the residues was determined by the somewhat modified method of I. V. Tananaev [5] (by distillation as H_2SiF_6). The HF content was determined by calculation of the quantity of fluorine bound as MnF_2 (Table 1, Fig. 1).

Apparently, at low HF concentrations, the solubility of $MnF_2 \cdot 4H_2O$ in hydrofluoric acid increases with an increase of the concentration of the latter; but since the equilibrium solubility of manganous fluoride is established very slowly, it is likely that some supersaturation is observed in the solutions.

The $MnF_2 \cdot 4H_2O$ is dehydrated by the action of alcohol at room temperature in a day (2.6% of water* was included in the residue). However, rapid washing with alcohol and ether, and removal of the latter at room temperature, enabled us to dry the crystal hydrate almost without loss of water:

	MnF_2 (%)	H_2O (%)
Sample 1	56.44	43.20
Sample 2	56.58	40.37
Theoretical	56.32	43.68

By this method it is possible to distinguish simply the anhydrous manganous fluoride and its hydrate. It was observed microscopically that the tetrahydrate precipitates as fine crystals (but coarser than the crystals of the anhydrous salt); their optical anisotropy was expressed much more sharply than was that of the anhydrous salt.

The method of the direct synthesis of $MnF_2 \cdot 4H_2O$ was incomparably simpler than that used by Nuka, Biltz and Rahlfs.

2. Solubility of MnF_2 and $MnF_2 \cdot 4H_2O$ in water. Transition point. Anhydrous MnF_2, in contact with water for several months at 15-19°, was almost completely converted to the hydrate. Consequently, the hydrate is stable at low temperatures. An attempt to determine the transition point of $MnF_{2\,cryst.} + 4H_2O \rightleftharpoons MnF_2 \cdot 4H_2O_{cryst.}$ by the thermometric method did not meet with success, since the reaction proceeds very slowly. The slowness of the conversion in both directions enabled us to determine the solubility of the anhydrous salt and the tetrahydrate, both in the stable region and also in the region of their metastable existence.

Mixtures of the salts and water were shaken in a thermostat; the manganese content was determined in the periodically-withdrawn samples of solutions. Saturation of the solutions, and conversion of the unstable form to the stable form, proceeded very slowly. For example, in a mixture of anhydrous MnF_2 and water at 0°, the maximum MnF_2 content in the solution (1.38%) was attained after 24 hours, but after 48 hours there was 1.296% more of MnF_2 in the

* Water was determined by drying at 120°. The method was not accurate enough because of the difficulties noted by Nuka.

solution, which was much more than the solubility of the tetrahydrate, which is stable at this temperature; in a mixture of tetrahydrate and water, shaken at 30° for 11 hours, no indication of dehydration was observed, although the anhydrous salt was stable under these conditions.

TABLE 2

Solubility and Calculated Activity of Saturated Solutions of Manganous Fluoride

Bottom phase	Temperature	Solubility (in %)	Solubility (in moles per 1000 g of water)	$-\log \gamma$	$\log \underline{a}$
$MnF_2 \cdot 4H_2O$	0°	0.800	0.0868	0.284	$\bar{1}.625$
	12	0.908	0.0977	0.276	$\bar{1}.744$
	20	0.970	0.1055	0.284	$\bar{1}.819$
	30	1.060	0.1150	0.292	$\bar{1}.912$
MnF_2	0	1.380	0.1505	0.316	$\bar{1}.187$
	20	1.060	0.1150	0.292	$\bar{1}.912$
	30	0.908	0.0977	0.276	$\bar{1}.744$

It should be noted that the MnF_2 suspension gradually turned brown on shaking, whereas the tetrahydrate suspension remained colorless. This can be accounted for by the fact that, the finer the crystals of the anhydrous salt, the more rapidly it is oxidized on the surface.

The solubility values, which we determined for the two forms of manganous fluoride, are cited in Table 2 and in Fig. 2, in which Nuka's data also are presented.

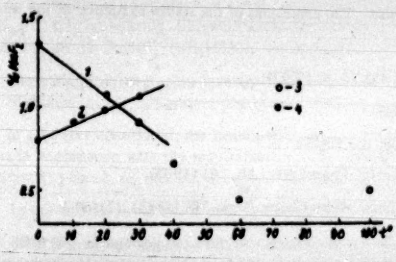

Fig. 2. Solubility of manganous fluoride. 1) MnF_2; 2) $MnF_2 \cdot 4H_2O$; 3) Nuka's data; 4) our data.

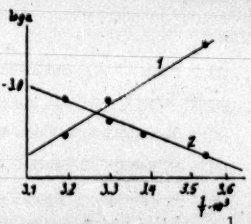

Fig. 3. Relationship of $\log \underline{a}$ to $\frac{1}{T} \cdot 10^3$. 1) MnF_2; 2) $MnF_2 \cdot 4H_2O$.

With the increase of temperature, the solubility of the tetrahydrate increases, but the solubility of the anhydrous salt decreases. The curves intersect at a temperature of about 23.5°, showing a transition point.

At 20°, the tetrahydrate solubility determined by Nuka was exaggerated, and was close to the anhydrous salt solubility which we found. Nuka's data were approximate values of the solubility at 40 and 60° and corresponded to the anhydrous form. The solubility value found by Nuka at 100° is incorrect.

The approximate values of the activity coefficients of saturated solutions of manganous fluoride ($\log \gamma$), cited in Table 2, were assumed to be equal to the activity coefficients of $MnCl_2$ solutions of the same molarity; these values were interpolated from data cited in the monograph of Harned and Owen [6]. By means of these calculated values, values of the activities of saturated solutions of manganous fluoride ($\log \underline{a}$) are also cited in Table 2.

The relation of $\log \underline{a}$ to $1/T$ (Fig. 3) was found to be almost linear. From the slope of the straight line, the average values of the heats of solution of MnF_2 and the tetrahydrate for the entire temperature interval was calculated. In connection with the low solubility of manganous fluoride, the latter and the integral heats of solution could not differ substantially. They were equal to 5.22 kcal/mole for MnF_2 and -3.75 kcal/mole for $MnF_2 \cdot 4H_2O$.

Consequently, the heat of hydration of MnF_2 by liquid water was equal to 8.97 kcal/mole. Using the value of the heat of vaporization of water (10.51 kcal/mole), it was easy to find the heat of dissociation of the tetrahydrate:

$$MnF_2 \cdot 4H_2O_{cryst.} \rightleftharpoons MnF_{2\,cryst.} + 4H_2O_{vapor} - 51.01 \text{ kcal.}$$

At the transition point, the dissociation pressure of the tetrahydrate was equal to the vapor pressure of the saturated solution; it can be calculated, knowing the vapor pressure of pure water and the concentration of the solution. The value of the dissociation pressure of the tetrahydrate was equal to 21.58 mm. Using the van't Hoff isochore, we were able to calculate that the dissociation pressure of the tetrahydrate at 20° was 16.66 mm. For the dehydration of the tetrahydrate at this temperature, it is sufficient to reduce the vapor pressure of the solution by 0.87 mm, and for this it is sufficient that the total concentration of the dissolved substances equal 2.75 moles per 1000 g of water. In the solution least concentrated in HF, used in the work of Kurtenaker and coworkers, the hydrofluoric acid concentration was equal to 2.8 moles per 1000 g of water; if, moreover, we take into account the dissociation of HF and the solubility of MnF_2, it becomes obvious that only the anhydrous manganous fluoride can be stable under the conditions employed by Kurtenaker.

Similar calculations showed that at 0° the tetrahydrate remains stable at a total concentration of dissolved substances of less than 14.8 moles per 1000 g of water. Therefore, in the above-described experiments of the direct synthesis of manganous fluoride tetrahydrate at 0°, it was shown to be the stable phase.

SUMMARY

1. A method was described for the direct synthesis of manganous fluoride tetrahydrate, by dissolving the carbonate in dilute hydrofluoric acid at 0°.

2. The solubility polytherms of anhydrous manganous fluoride and its tetrahydrate were determined. The transition point was at 23.5°. The conversion of each form to the other occurred very slowly.

3. The heats of solution of both forms of manganese fluoride, the heat of hydration of the anhydrous salt, and the heat of dissociation of the tetrahydrate were calculated. The conditions of the stable existence of the tetrahydrate were investigated.

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TRANSFORMATION OF COBALTAMMINE NITRITES BY HEATING IN THE SOLID STATE

A. V. Ablov and N. I. Lobanov

The reactions of the most stable complex compounds, namely, of platinum and trivalent cobalt, have been rather completely studied in solutions. Very little work has been devoted to transformations in the solid state.

The conversion of tetrammine platino-salts $[Pt(NH_3)_4]X_2$ to platinum trans-diacidodiammine is very well known. L. A. Chugaev and S. S. Kiltynovich [1] found that at 100° dry nitrotriammine platinonitrite $[Pt(NH_3)_3(NO_2)]NO_2$ is almost quantitatively converted to platinum trans-dinitrodiammine with the liberation of one molecule of ammonia.

A. A. Grinberg and B. V. Ptitsyn [2] studied the thermal stability of the tetrammine platino-salts. On heating, the latter are converted to platinum trans-diacidodiammine. The ease of conversion increases in a series from chloride to bromide, nitrite and, finally, to iodide. A. A. Grinberg explained the fact that he was unable to detect the intermediate decomposition products

$$[Pt(NH_3)_4]X_2 \xrightarrow{-NH_3} [Pt(NH_3)_3X]X \xrightarrow{-NH_3} [Pt(NH_3)_2X_2],$$

by the lower stability of the triammine salt in comparison with the tetrammine salt. Thus, for example, the tetrammine nitrite $[Pt(NH_3)_4](NO_2)_2$ begins to decompose at 145°, but the triammine nitrite $[Pt(NH_3)_3NO_2]NO_2$, at 137°.

In a number of compounds of quadrivalent platinum, L. A. Chugaev found that the chloropentammine chloride, $[Pt(NH_3)_5Cl]Cl_3$, on heating, liberated ammonia and was converted to trans-dichlorotetrammine platinochloride. The tetrammine amide $[Pt(NH_3)_4(NH_2)Cl]Cl_2$ was obtained as a by-product.

Interesting thermographic investigations of the complex compounds of platinum and palladium were made by A. V. Nikolaev, A. M. Rubinshtein and others [3, 4].

In all cases considered, the introduction of an acid radical into the internal sphere of the platinic complex occurs in accordance with the requirement of I. I. Chernyaev's trans-effect rule, although, as A. A. Grinberg and B. V. Ptitsyn [2] noted, on thermal decomposition, the influence of the trans-effect is very weakly expressed.

In the literature we found only two works on the thermal decomposition of the cobaltammines.

Biltz [5], on heating hexammine cobaltichloride in an atmosphere of ammonia at about 202°, observed its conversion to chloropentammine cobaltichloride, but on heating to temperatures above 225° there was decomposition of the substance, with the reduction of trivalent cobalt to the bivalent form.

Clark, Quick and Harkins [6] studied the heating of hexammine cobaltichloride, nitropentammine cobaltichloride and cobalt trinitrotriammine. They found that for hexammine cobaltichloride, the liberation of ammonia began at 173°; but at 181°, decomposition set in with the formation of an efflorescence of ammonium chloride. For nitropentammine cobaltichloride, a slight evolution of gas was observed at 100°, and a rapid evolution of gas began at 210°, in which the gas consisted of nitrogen and ammonia. At 158°, cobalt trinitrotriammine began to evolve gas, and at 164°, there was sudden decomposition, with the formation of nitrogen, water and Co_2O_3.

From the works cited, it can be concluded that the cobaltammines are not resistant to heating at temperatures above 160-180°. On the other hand, for the luteochloride it is obvious that within small temperature intervals the evolution of one molecule of ammonia, with the formation of the purpureochloride, occurs.

The circumstance that ammonia, occurring in the trans-position to chlorine, is not further replaced by chlorine with the formation of trans-dichlorotetrammine cobaltichloride, does not fall within the framework of the trans-effect rule.

This circumstance induced us to undertake a study of the reactions which occur on heating the cobaltammines in the solid state.

It is known that in the cobalt nitropentammine cation, on heating in solution with nitrite-ion, there is a replacement of ammonia, found in the trans-position to the nitro-group, by the NO_2-group and the formation of the cobalt trans-dinitrotetrammine cation [7].

It was of interest to investigate whether a similar reaction would proceed on heating nitropentammine cobaltinitrite in the crystalline state.

The experiments set up showed that the heating of dry nitropentammine cobaltinitrite for several hours at a temperature no higher than 140-145° led to a loss of ammonia by the solid salt. Ammonia, displaced from the internal sphere of the nitropentammine cobaltinitrite, should be replaced by the nitro-group. It was natural to assume that, just as in the aqueous solution, trans-dinitrotetrammine cobaltinitrite (crocenonitrite) was the decomposition product.

However, it was found that a heterogeneous product was obtained on heating, and that it could be separated into two fractions: a product which was readily soluble in cold water and one which was difficultly soluble. It was shown that the readily soluble fraction did not undergo alteration to the xanthonitrite. The difficultly soluble fraction – a light-yellow substance – was recrystallized from water acidified with acetic acid.

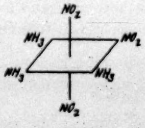

Fig. 1. Configuration of cobalt trinitrotriammine.

Measurement of the electrical conductivity of the difficultly soluble fraction showed that the substance was a non-electrolyte. The Debye photograph gave an entirely clear picture, which showed complete coincidence of the lines of the substance investigated with the lines of synthetic cobalt trinitrotriammine.

Thus, it was demonstrated that nitropentammine cobaltinitrite, on heating, liberated two molecules of ammonia and was converted to cobalt trinitrotriammine.

We adopted 1,2,6, with two nitro-groups in the trans-position, as the most likely configuration of cobalt trinitrotriammine. This assumption recently received confirmation in the work of G. B. Boky and E. A. Gilinskaya [8], who, on the basis of an X-ray study, established a trans-configuration for the $[Co(NH_3)_2(NO_2)_4]^-$ ion. On the other hand, Dhar [9], by heating cobalt trinitrotriammine with a concentrated solution of potassium nitrite, converted it to Erdman's salt $K[Co(NH_3)_2(NO_2)_4]$. The latter reaction can be understood by attributing the trans-configuration to cobalt trinitrotriammine. However, it should be noted that the possibility of isomerization on heating cobalt trinitrotriammine in solution was not excluded. In any case it is fundamental to assume that cobalt trinitrotriammine actually has the configuration shown in Fig. 1.

Concerning the mechanism of the conversion of nitropentammine cobaltinitrite on heating, it can be assumed that a replacement of ammonia by the nitro-group takes place in two steps, and that cobalt dinitrotetrammine (cis- or trans-) ion forms as the by-product.

Neither the croceo-ion, nor the flavo-ion was observed in the product of the heating of the xanthonitrite. However, the possibility of their formation as unstable intermediate compounds, as proposed by A. A. Grinberg and B. V. Pritsyn for the thermal decomposition of tetrammine platinonitrite [2], was not excluded.

A further investigation led to an extremely curious fact, and proved precisely that on heating 1,6-dinitrotetrammine cobaltinitrite the introduction of a nitro-group into the complex does not occur. On the other hand, the heating of 1,2-dinitrotetrammine cobaltinitrite (flavo-) led to the formation of a high yield of cobalt trinitrotriammine.

These facts may be explained, starting from the trans-effect rule of I. I. Chernyaev.

Ammonia, occurring in the trans-position to the nitro-group in the flavo-ion, is bound less stably to the central atom. On heating in a range of intense heat, it breaks up and leaves the nucleus of the complex, and the freed space is occupied by the nitrite-ion from the crystal lattice.

In the croceo-salt no ammonia molecule is found in the trans-position to the nitro-group. All the ammonia molecules are bound equally securely to the central cobalt atom and the loss of ammonia from the inner sphere may occur at the higher temperatures, at which the compound decomposes.

As to the reactions which the xanthonitrite undergoes, they can be explained by the fact that (Fig. 2), as the most labile, ammonia (6), which occurs in the trans-position to the nitro-group, breaks away on heating. If the reaction takes place in an aqueous medium at a high nitrite-ion concentration, then the nitro-group occupies position (6)

with the formation of the croceo-salt. Under conditions of heating the dry salt, the NO_2-ion from the crystal lattice is unable to occupy this position. Ammonia molecule (2), which occurs in the inner sphere of the complex takes it over, whereupon isomerization occurs, and the NO_2-ion from the crystal lattice now occupies the freed position (2) [10].

The fact that we were unable to detect flavonitrite in the product from the heating of xanthonitrite may be accounted for by the fact that the decomposition of flavonitrite proceeds more readily than does that of the xantho-

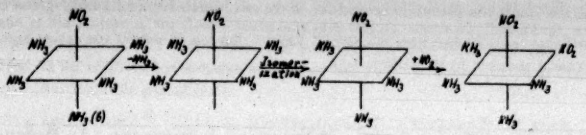

Fig 2. Mechanism of transformation of nitropentammine cobaltinitrite by heating.

nitrite. Actually as our data will confirm, at a given time and also under the same conditions of heating, the relative amount of flavonitrite which undergoes reaction is larger than that of the xanthonitrite. Thus, for example, in experiment 1 (Table 1), the quantity of xanthonitrite which underwent reaction in 17 hours was about 66%, whereas about 89% of the flavonitrite (Table 4, experiment 3) underwent reaction in 12 hours.

The heating of hexammine cobaltinitrite at the same temperature as used for the heating of the nitrites described earlier gave an interesting result. It was shown that also in a very stable and symmetrically constructed complex there is replacement of an ammonia molecule by a nitro-group. As a result, cobalt trinitrotriammine forms here also. In this case, it can be assumed that decomposition proceeds via the xanthonitrite.

As may be judged from a comparison of our data with Clark's data, the loss of ammonia by hexammine cobaltinitrite proceeds at a lower temperature than for the chloride, i.e., the NO_2-group is more easily introduced into the inner sphere than is chlorine. On the other hand, the fact that for the xanthochloride the evolution of gas begins at a temperature of about 100°, undoubtedly indicates the strong trans-effect of the nitro-group. A. A. Grinberg and B. V. Pritsyn [2] have indicated the significance of these two factors in the thermal decomposition of the ammines of platinum.

The displacement of ammonia by acid radicals, on heating the cobaltammines becomes observable at temperatures which only sometimes lie below the temperature of complete decomposition of the cobaltammine. The cobaltammine nitrites which we studied were very interesting in this respect, since they did not undergo decomposition at temperatures of 130-140°, but the ammonia molecules were slowly replaced by NO_2-ions.

Although the heating of dry nitrites does not lead to introduction of more than three nitro-groups this is possible possible in solutions. However, as Bailar and Work [11] showed, the heating of an aqueous solution of hexammine cobalti-ion with sodium nitrite in the presence of carbon, leads to the formation of cobalt trinitrotriammine. On the other hand, in the presence of the same catalyst, the heating of sodium cobaltinitrite with ammonia water also leads to cobalt trinitrotriammine. Cobalt trinitrotriammine is more stable in an aqueous system; however, this does not seem to be a decisive factor in the occurrence of the reaction in the dry state, since the croceonitrite is not converted to cobalt trinitrotriammine, or its transition may be accomplished at a higher temperature, at which the decomposition of the substance should occur.

Thus, not the thermal stability of the final product, but the capacity of the groups in the complex for substitution reactions, as required by the trans-effect rule, predetermines the course of the reaction.

EXPERIMENTAL

The cobaltammine nitrites were prepared by a method described in the literature. The air-dry products were heated in a drying chamber at 105°; in this way, they lost hygroscopic moisture and the croceonitrite also lost its water of crystallization.

A weighed portion of the substance to be studied was placed in a conical flask covered with a rubber stopper fitted with two tubes, one of which reached almost to the bottom of the flask, and the other was short. Air was slowly (one bubble per second) drawn by an aspirator through the flask, and later passed through another flask in which

there was a measured quantity of a titrated solution of sulfuric acid. The flask and the substance to be investigated were heated on an oil bath at a temperature, as a rule, not exceeding 145°, since in some experiments an increase of the temperature, even for a short time to 150°, leads to decomposition. Under the condition that the oil bath temperature at the time of the experiment not exceed 150°, the loss in weight of the salts was equal (within the limits of experimental error) to the quantity of ammonia carried away by the current of air and that entrapped by the titrated solution of sulfuric acid.

1. Heating of nitropentammine cobaltinitrite. The results of the heating of this salt are cited in Table 1. On heating the dark-yellow xanthonitrite at a moderate temperature (not above 140°), its color faded. At a higher temperature (about 150°) there was partial decomposition of the salt, which assumed a dirty-green color.

In the first case, as is evident from the data of Table 1, the loss in weight was rather high, compared with the quantity of ammonia absorbed by the sulfuric acid.

TABLE 1

Expt. No.	Weighed portion (in g)	Temperature of oil bath	Heating time (in hours)	Weight loss (in g)	Quantity of NH_3 absorbed (in g)
1	2.561	130-135°	17	0.202	0.189
2	1.495	130-140	6	0.143	0.137
3	1.467	140-150	8	0.128	0.117
4	1.388	140-150	8	0.135	0.117
5	3.209	150-160	8	0.391	0.249

The product which remained in the flask after heating, from Experiment 1, was mixed well, and its ammonia content (23.4% NH_3) was determined. The result of the analysis corresponded to a weight loss of 0.173 g of ammonia, 0.189 g was absorbed by sulfuric acid; as is obvious, these values agree adequately.

It should be noted that, the higher the temperature at which the heating of the xanthonitrite was carried out, the larger the significant difference between the ammonia by loss in weight and the ammonia by quantity absorbed (Experiment 5).

It was observed that the product of the heating was not homogeneous, and it could be separated into two fractions: one fraction which was readily soluble in cold water, unaltered xanthonitrite, and another which was very difficultly soluble.

The method of separation was the following: the product from the heating was transferred to a fine filter and washed several times with as small quantities of cold water as possible, until it was seen that the readily soluble fraction, which formed a solution of a darker color, was completely removed. The readily soluble fraction was precipitated from the filtrate, by alcohol, as a finely-crystalline yellow precipitate. The readily soluble fraction (from the combined batches in Experiments 3 and 4) gave a qualitative reaction for the presence of nitrite-ion and xantho-ion and for the absence of flavo- and croceo-ions.

A determination of the electrical conductivity* at 25° and at a dilution of v = 1376 gave a value of μ 282 Ω^{-1} cm^2; a value of μ 234.4 at v = 1000 and μ 242.8 at v = 2000 was cited in the literature [12].

The difficultly soluble fraction (Experiments 3 and 4) was washed well with water, then with alcohol and ether, and was recrystallized from water which contained a little acetic acid. The determination of the electrical conductivity of this fraction at 25° and v = 1203 gave a value of μ 25 Ω^{-1} cm^2, which indicated a somewhat contaminated non-electrolyte. From the crystal form and solubility, it could be assumed that this substance was ordinary cobalt trinitrotriammine.**

A Debye photograph (Table 2) showed complete coincidence of the lines of the substance studied with the lines of cobalt trinitrotriammine synthesized by Jörgensen's procedure [13].

Qualitative reactions, for example, like the dichro-reaction [14], also showed the complete identity of the difficultly soluble fraction with cobalt trinitrotriammine.

* The xanthonitrite which was precipitated by alcohol contained no water of crystallization.

** The non-recrystallized, difficultly soluble fraction had an electrical conductivity of μ 124 Ω^{-1} cm^2 (25°) at v = 1000.

The Debye photograph of the difficultly soluble fraction, recrystallized from water which contained acetic acid, showed the same lines as did synthetic cobalt trinitrotriammine (Table 2).

The difficultly soluble fraction was washed carefully. A cobalt determination showed a composition of $[Co(NH_3)_3(NO_2)_3]$.

0.1510, 0.1446 g sub.: 0.2974, 0.2818 g $CoPy_4(CNS)_2$. Found %: Co 23.64, 23.38. Calculated %: Co 23.76.

For a more complete identification of the difficultly soluble fraction, 2 g of the product was covered with 20 ml of a concentrated hydrochloric acid. After a short time, the substance acquired a cinnamon-red color. On the next day the small flask and its contents were submerged for a short time in boiling water. An evolution of brown nitrogen oxides resulted, and at the bottom of the flask a green substance formed, which was filtered off, washed several times with dilute hydrochloric acid (1:1) and alcohol, and later dissolved in 30 ml of cold water. To the dark-violet solution we added 20 ml of dilute hydrochloric acid in two portions. On the next day well-bounded crystals of triaquatriammine cobaltichloride precipitated.

0.0843 g sub.: 0.1384 g AgCl. Found %: Cl 40.62. $[Co(NH_3)_3(H_2O)_3]Cl$. Calculated %: Cl 39.33.

After removal of the dark-violet crystals of triaquatriammine cobaltichloride we added 20 ml of concentrated hydrochloric acid to the filtrate. Dark green crystals precipitated gradually, and were filtered off and washed with dilute hydrochloric acid and alcohol.

0.1119 g sub.: 0.2046 g AgCl. Found %: Cl 45.24. $[Co(NH_3)_3(H_2O)Cl_2]Cl$. Calculated %: Cl 45.40.

Thus, it was demonstrated that the difficultly soluble fraction was actually cobalt trinitrotriammine.

4. Heating of hexammine cobaltinitrite. The heating of the luteonitrite was carried out at three temperature intervals (Table 5).

TABLE 5

Expt. No.	Weighed portion (in g)	Oil bath temperature	Heating time (in hours)	Weight loss (in g)	Quantity of NH_3 absorbed (in g)
1	1.748	130-135°	20	0.154	0.145
2	6.504	135-140	24	0.829	0.733
3	2.644	140-145	24	0.414	0.301

In this case we also observed that an increase of the temperature above 135° led to a partial decomposition of the luteonitrite. Only in the 130-135° interval was there good agreement of the weight loss with the quantity of ammonia absorbed.

In the same way as in the above described experiments of heating the flavo- and xanthonitrites, the product from the luteonitrite was heterogeneous. The readily and difficultly soluble fractions were separated by the method described above. The readily soluble fraction gave all the characteristic reactions of the luteo-ion, but showed no reactions for xantho-, flavo- or croceo-ions. The difficultly soluble fraction was washed carefully with water, then with alcohol and ether, and was analyzed.

0.1661, 0.2021 g sub.: 0.3233, 0.3979 g $CoPy_4(CNS)_2$. Found %: Co 23.36, 23.62. 0.2188 g sub.: 0.0459 g NH_3. Found %: NH_3 20.97. 0.02502 g sub.: 7.48 ml N_2 (21°, 754.5 mm). Found %: N 34.18. $[Co(NH_3)_3(NO_2)_3]$. Calculated %: Co 23.76; NH_3 20.56; N 33.89.

The substance, recrystallized from water which contained a little acetic acid, gave a Debye photograph, the lines of which agreed completely with those of the Debye photograph for synthetic cobalt trinitrotriammine.

A small quantity of the difficultly soluble fraction was covered with concentrated hydrochloric acid and heated in boiling water. The yellow powder was converted to a light yellow substance, which was filtered off, and washed with dilute hydrochloric acid and alcohol.

A determination of chlorine in this substance showed conclusively that the dichro -chloride formed in this instance.

In conclusion, the authors of the article regard it as their pleasant duty to thank T. I. Malinovsky for his kind assistance in taking the Debye photographs.

TABLE 2

$[Co(NH_3)_2(NO_2)_3]$		Difficultly soluble fraction after heating and recrystallization					
		xanthonitrite		flavonitrite		luteonitrite	
I	D	I	d	I	d	I	d
	–		–		–	3	6,71
5	6,42	5	6,42		–	4	6,51
5	6,03	5	6,00		–	8	6,03
5	5,80	8	5,80		–	10	5,79
8	5,58	8	5,58	10	5,57	6	5,62
5	5,22	5	5,19	8	5,21	8	5,28
10	5,01	10	5,04	7	5,14	10	5,07
5	4,60	5	4,62	5	4,58	5	4,62
7	4,04	7	4,04	5	4,06	7	4,04
8	2,93	8	2,93	7	2,94	8	2,93
	–	3	2,66	3	2,69	3	2,68
	–	6	2,48	6	2,48	5	2,49
	–	2	2,16	4	2,22	3	2,21
	–	3	2,03	4	2,04	3	2,11
	–	3	1,92	3	1,91	3	1,92

2. Heating of 1,6-dinitrotetrammine cobaltinitrite. The heating experiment showed that the behavior of the croceonitrite was different from that of the xanthonitrite. The salt, heated for 12 hours at 130-135°, lost about 1% in weight, after which decomposition occurred.

TABLE 3

Weighed portion (g)	Oil bath temperature	Heating time (hrs)	Weight loss (g)	Quantity of NH_3 absorbed (g)
1,849	130-135°	12	0,019	0,012

From the data cited in Table 3 it is evident that the loss in weight exceeded the quantity of ammonia liberated by more than 50%. The substance acquired a dirty greenish-yellow color as a result of the heating. On treatment with water which contained a small amount of acetic acid, an insoluble deposit of cobaltic oxide was obtained.

Qualitative reactions made on the filtrate showed the presence of undecomposed croceo-ion only.

1.732 g of the product from the heating was acted on by a weak acetic acid solution, and the filtrate was precipitated by ammonium sulfate. 1.473 g of the croceosulfate was obtained, which corresponded to 1.462 g of the croceonitrite.

Thus, it should be assumed that the croceonitrite was not changed by the introduction of the NO_2-group into the internal sphere.

3. Heating of 1,2-dinitrotetrammine cobaltinitrite. The heating was carried out at two temperature intervals 130-135° and 135-140° (Table 4).

TABLE 4

Expt. No.	Weighed portion (in g)	Oil bath temperature	Heating time (in hours)	Weight loss (in g)	Quantity of NH_3 absorbed (in g)
1	1,328	130-135°	6	0,053	0,051
2	1,172	130-135	6	0,025	0,024
3	1,101	130-135	12	0,064	0,062
4	3,437	130-140	16	0,197	0,169

It should be noted that a higher temperature and longer heating (Experiment 4) led to some decomposition of the complex; apparently, nitrogen and water, in addition to ammonia, were liberated.

The product from the heating of the flavonitrite was heterogeneous, since on treatment with cold water two fractions separated, a readily soluble one representing undecomposed flavonitrite, and another fraction which was difficultly soluble in water.

SUMMARY

1. The behavior of the cobaltammine nitrites – hexammine cobaltinitrite, nitropentammine cobaltinitrite, and the two isomeric dinitrotetrammine cobaltinitrites – on moderate heating in the dry state was studied.

2. The nitrites of the hexammine, nitropentammine, and cis-dinitrotetrammine series, on heating in the solid state, lost ammonia from the internal sphere, replacing it by nitro-groups, Cobalt trinitrotriammine was the reaction product in all cases.

3. Trans-dinitrotetrammine cobaltinitrite did not undergo such reactions on heating.

4. The difference in behavior of the cobaltammine nitrites may be accounted for on the basis of I. I. Chernyaev's trans-effect rule.

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SEPARATION OF SMALL QUANTITIES OF COBALT FROM SOLUTIONS

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In the electrolytic production of zinc, the original solution of zinc sulfate contains a number of impurities. Some of them, for example, cadmium and copper, are separated from the electrolyte not only in order to obtain pure zinc, but also as components of known value. Some of the impurities, to which arsenic, antimony, cobalt and germanium belong, are necessarily removed beforehand because they are undesirable impurities in the zinc obtained, and especially because in their presence electrolysis is almost impossible.

The removal of arsenic and antimony is rather easily solved by different methods, to which belongs their joint precipitation with ferric hydroxide or zinc oxide. Methods of cementation by iron, zinc dust and aluminum give positive results.

The freeing of the electrolyte from cobalt presents a great difficulty. Of the known methods for freeing the zinc sulfate solution from cobalt, a method proposed by M. A. Ilyinsky find application in industrial practice. This method includes the fact that, by the action of a solution of β-naphthol on a cobalt-containing solution, in the presence of sodium nitrate, a precipitate of cobalt α-nitroso-β-naphtholate is obtained. At best the cobalt concentration in the solution is reduced to 2-3 mg/liter, by continuation of the process for about 4 hours [1]. Practically the cobalt content remaining in the solution is usually no lower than 5 mg/liter. There are also other methods for the separation of cobalt [2], for example, the xanthogenate method.

For carrying out the industrial process, and also for research purposes, it is necessary to carefully control the cobalt content in solution. Cobalt is most conveniently removed from solution as a precipitate, and its quantity is determined later. The precipitation of cobalt as the α-nitroso-β-naphtholate is unsuitable, because of the length of the process of precipitation and the incompleteness of separation of cobalt from the solution. The method of separation of cobalt by cementation was investigated at length recently by G. S. Frents and B. P. Kreingauz [3], and also by D. M. Chizhikov and B. P. Kreingauz [4]. It is evident from these investigations that on cementation, a certain quantity of cobalt (20-30 mg/liter) always remains in solution. These investigations were carried out with solutions containing a relatively large quantity of cobalt, from 3 to 0.55 g/liter. From the data cited in the work of G. S. Frents and B. P. Kreingauz [3], it is evident that cementation gave a smaller content of cobalt in solution, the lower the initial quantity of cobalt.

Calculation on the basis of the Nernst formula showed [3] that at equilibrium $\frac{[Zn^{++}]}{[Co^{++}]} = 3{,}56 \cdot 10^{16}$, where $[Zn^{++}]$ and $[Co^{++}]$ are the ionic concentrations of the corresponding metals in solution, in the presence of the metallic pair zinc–cobalt. Hence, it follows that the cementation of cobalt by metallic zinc should proceed until the concentration of zinc ions in solution becomes no more than $3{,}56 \cdot 10^{16}$ times greater than the concentration of the cobalt ions, i.e., the process of displacement of cobalt by zinc should go to completion.

EXPERIMENTAL

Starting from this, we set up experiments on the cementation of cobalt from a solution of zinc sulfate. Quantitative determination of cobalt was made by the radioactive indicator method, for which we introduced into the original solution cobalt sulfate, which contained a certain quantity of the radioactive isotope of cobalt Co^{60}. Measurement of the Co^{60} activity was made for gamma-emission by a cylindrical counter with aluminum walls.

For the measurements, 5 ml of solution was withdrawn and placed in a glass cuvette, which was mounted in a precisely fixed position near the counter. The activity value of the preparation was expressed in counts per minute. Each sample was measured several times, and a measurement of the background was made before and after each determination. Into the data obtained we introduced corrections for the background value, which fluctuated within the limits of 20-22 counts per minute, and for the dead time of the counting apparatus. The average activity value was calculated from the data obtained. The error of the activity measurements did not exceed ±5% for activity measurements above 100 counts per minute, and ±10% for activity measurements within the limits from 100 to 30 counts per minute.

The original solution contained 110 g/liter of zinc and 5 mg/liter of cobalt as the sulfates. The activity of the original solution was equal to 7230 counts per minute. 0.5 g of zinc dust was added to 10 ml of such a solution, and the mixture was shaken for 60 minutes. The precipitate was filtered off, and the activities of the solution and the precipitate were measured. The activity of the precipitate was not measured directly, but the precipitate was first dissolved in acid and the solution was diluted to 10 ml.

The ratio of the activities indicated the distribution of cobalt between the solution and the precipitate. It was found that practically all of the cobalt remained in the solution. Similar results were obtained on cementation of cobalt from such a solution by aluminum powder. The aluminum powder absorbed 13-14% of the cobalt from the solution (Table 1).

An opinion [1] exists that it is possible to increase the separation of cobalt from zinc, if copper, cadmium, arsenic or tellurium is separated simultaneously with cobalt. In this case, precipitation of cobalt should be more complete, due to the energy of formation of cobalt compounds with arsenic or tellurium, or due to the energy of formation of a melt with copper or cadmium.

Application of the data confirmed this position; however, the reduction of the cobalt concentration did not exceed the limit at 10-5 mg/liter [1].

TABLE 1

Time of Cementation 1 hour

Precipitant	Activity, in counts per minute		Cobalt extracted from the solution (%)
	solution	precipitate	
Zinc dust	7157	43	0.6
Zinc dust	7112	34	0.5
Aluminum powder	6328	810	13
Aluminum powder	6345	880	14

We used an oxidizing agent for the separation of cobalt as the hydroxide of trivalent cobalt. However, this method gave undecipherable results, since its use involved the necessity of maintaining a number of conditions which were decisive. The oxidation potential of trivalent cobalt increases in proportion to the concentration increase of the hydrogen ions (reduction of pH of the solution). The stability of trivalent cobalt increases at the higher pH's; therefore, a higher pH value of the solution is possibly an essential condition for obtaining positive precipitation results. The highest pH was obtained for the zinc electrolyte in equilibrium with zinc oxide. In this case, when the zinc concentration in the solution reaches 100 g/liter, the pH of the solution in equilibrium with zinc oxide will be almost 5.

The relatively high solubility of the hydroxide of trivalent cobalt, which according to one literature datum was equal to 0.01046 mg/liter [5], but according to another reached 3.2 mg/liter [6], which correspond to 0.0056 and 1.7 mg/liter of cobalt, might impede the complete separation of cobalt. Because of this, the separation of the hydroxide of trivalent cobalt should be carried out jointly with some other precipitate capable of separating under these conditions, for example, manganese dioxide, which is formed by the oxidation of bivalent manganese.

The oxidizing agent should be chosen by the criterion of the highest positive value of its oxidation potential. It is always necessary to employ a certain excess of oxidizing agent, since the manganese dioxide which remains unoxidized inevitably reduces the trivalent cobalt.

The conditions indicated were examined. For this a solution containing manganese sulfate, zinc sulfate and cobalt sulfate was prepared. The concentrations of the components corresponded to: 110 g/liter of zinc, 1.25 g/liter of manganese and 5 mg/liter of cobalt. For checking the quantity of cobalt we used the radioactive indicator method, the application and accuracy of the operation of which were described earlier. The activity of the original solution was 6830 counts per minute.

To 10 ml of the original solution, we added zinc oxide, an oxidizing agent, and, if the process of oxidation required an increase of temperature, we warmed up the solution. The oxidation was carried out with stirring in order to keep the zinc oxide in the suspended condition. On completion of the oxidation process, the precipitate was filtered off through a dry filter, and the filtrate was collected. The precipitate and filtrate were analyzed for their cobalt contents by measurement of the radioactivity. The quantity of cobalt remaining in solution and the percentage of cobalt recovered were calculated from the activity values of the solution and precipitate.

Reactions were investigated with the following oxidizing agents: potassium permanganate, potassium chlorate and potassium persulfate (Table 2).

TABLE 2

Test No.	Name of oxidizing agent	Quantity (in g)		Temperature	Activity (in counts per minute)		Cobalt concentration in solution after precipitation (in mg/liter)	Cobalt extracted (in %)
		oxidizing agent	zinc oxide		solution	precipitate		
1	Potassium permanganate	0.1	–	20°	5694	1260	4.1	18
2		0.1	–	100	5708	1275	4.1	18
3		0.02	0.1	20	5921	790	4.4	12
4		0.02	0.1	100	6111	720	4.5	10
5		0.05	0.1	20	614	6440	0.43	91
6		0.1	0.1	20	3	6710	< 0.05	> 99
7		0.1	0.1	100	6	6650	< 0.05	> 99
8	Potassium chlorate	0.1	–	100	6528	380	4.7	5
9		0.1	0.1	100	17	6860	< 0.05	> 99
10		0.2	0.1	100	12	6713	< 0.05	> 99
11	Potassium persulfate	0.2	–	100	6222	510	4.6	10
12		0.05	0.1	100	6248	670	4.5	10
13		0.2	0.1	100	10	6800	< 0.05	> 99
14		0.2	0.1	100	14	6765	< 0.05	> 99
15		0.4	0.1	100	86	6620	0.06	99

As is evident from Table 2 (Experiments 6, 7, 9, 10, 13, 14 and 15), in the presence of zinc oxide, i.e., at a suitable pH of the solution, and by the use of an excess of oxidizing agent, we can obtain a practically complete extraction of cobalt from the solution, if it is precipitated jointly with manganese dioxide.

Cobalt is scarcely precipitated (Experiments 3, 4 and 12), if the precipitation is carried out with insufficient oxidizing agent, i.e., when bivalent manganese remains in the solution. The cobalt is scarcely retained by manganese dioxide in the absence of zinc oxide (at lowered pH values of the solution), in spite of the excess of oxidizing agent.

The oxidation of bivalent manganese by persulfate and chlorate required heating above 70°. The oxidation process proceeds rather slowly. The relation of the completeness of the extraction of cobalt to the duration of action of the oxidizing agent was evident from the following experiment. After addition of zinc oxide, potassium persulfate was added to 40 ml of a solution of the same composition which was used in the preceding experiments. The solution was heated on the water bath, after which samples were withdrawn after 10, 20 and 80 minutes. The activities of the solutions were equal to 6753, 143 and 31 counts per minute, respectively. Thus, after 10 minutes no passage of cobalt from the solution to the precipitate was noted, after 20 minutes a total of 2.1% of the cobalt remained in the solution, but after 80 minutes 0.45%, i.e., practically all of the cobalt had been precipitated from the solution.

Apparently the slowness of the oxidation of bivalent manganese, which proceeds for more than 10 minutes, may serve as the explanation of this. During this time cobalt is not oxidized, and therefore, in spite of the formation of a precipitate, it remains in solution. It is likely that in the time that follows the incompleteness of the extraction of cobalt is determined by the fact that the highly-dispersed manganese precipitate, forming a colloidal solution, passes through the filter, and together with it also cobalt. An almost complete absence of cobalt was observed in the solution after complete coagulation of the precipitate.

From the results cited, it follows that all of the cobalt may remain in solution, if the oxidation of bivalent manganese is not carried to completion, since in the presence of bivalent manganese the oxidation of cobalt is almost excluded.

Severald additional experiments were carried out in order to verify this.

1. Precipitates obtained by the method described earlier were dissolved in a mixture of solutions of oxalic and sulfuric acids. A large part of the manganese was precipitated from the solution by the action of an insufficient quantity of oxidizing agent (Table 3).

TABLE 3

Expt. No.	Oxidizing agent	Temperature	pH of solution	Activity of solution: original	Activity of solution: after precipitation	Quantity of cobalt in solution after precipitation of manganese (in %)
1	Potassium permanganate	20°	2	5005	4857	97
2		20	5	7290	6716	92
3	Potassium persulfate	100	2	3578	3556	99
4		100	5	3560	3237	91

In Experiments 2 and 4 (Table 3) the process was carried out in the presence of zinc oxide. As is evident from the data of Table 3, with a deficiency of oxidizing agent, cobalt remained almost completely in solution, not only at low pH but also in the presence of zinc oxide (pH ~5).

2. The precipitates containing cobalt were washed with a solution of a salt of bivalent manganese. With an acidified solution of manganese sulfate we were able to wash out about 80% of the cobalt.

In order to establish more accurately whether zinc oxide was only a regulator of the pH of the solution or whether it might play a role as an adsorbent, we carried out the separation of cobalt from solutions in the presence of zinc oxide and zinc hydroxide, in the absence of manganese dioxide, and also in the presence of manganese dioxide and an excess of oxidizing agent, but without zinc oxide and with the use of a buffer solution.

For the experiments carried out in the absence of manganese dioxide (Table 4), a solution of zinc sulfate containing 100 g/liter of zinc and 5 mg/liter of cobalt was prepared. Zinc sulfate was freed from impurities by addition of alkali to the solution until the formation of an appreciable quantity of precipitate and hydrogen peroxide. After boiling, the precipitate was filtered off, and cobalt sulfate containing an admixture of the radioactive isotope of cobalt was added to the filtrate. In Experiments 1 and 2 (Table 4) zinc oxide was added to the solution, in Experiments 3 and 4 – freshly precipitated zinc hydroxide; in Experiments 5 and 6 – alkali.

TABLE 4

Expt. No.	Composition of original solution	Conditions of precipitation of cobalt	Activity (in counts per minute): original solution	Activity (in counts per minute): filtrate	Activity (in counts per minute): precipitate	Cobalt extracted from solution (%)
1	100 g/l of zinc and 5 mg/l of cobalt	To 10 ml of solution, 0.1 g of zinc oxide was added	4560	4001	669	15
2			4560	4429	76	2
3		To 10ml of solution, 0.01 g-equiv of zinc hydroxide was added	4560	4136	496	10
4			4560	3475	1261	30
5		To 10 ml of solution, 0.01 g-equiv of sodium hydroxide was added	4560	–	751	15
6			4560	–	1009	20
7	5 mg/l of cobalt, 1.25 g/l of manganese sulfate	Acetate buffer with pH 4.6	4420	230	4175	95
8			4420	87	4210	98

In the experiments carried out in the presence of manganese dioxide, but in the absence of zinc oxide of hydroxide, with the use of a buffer solution, the solution contained 5 mg/liter of cobalt with an admixture of radioactive isotope, 1.25 g/liter of manganese sulfate, 6 g/liter of acetic acid and 8.2 g/liter of sodium acetate. The solution had a pH of 4.6. In each of the experiments, 0.2 g of potassium persulfate was added to 10 ml of the original solution, it was boiled, and the precipitate was then filtered off. The activities of the original solution, the filtrate and the precipitate were measured as described earlier.

As is evident from the data of Table 4, in Experiments 1-6 we were unable to attain complete transference of cobalt to the precipitate in the absence of manganese dioxide, in spite of the presence of an excess of oxidizing agent, the presence of zinc oxide or hydroxide, and a sufficiently high pH value of the solution (~5). In the presence of manganese dioxide (Experiments 7 and 8) at a pH of 4.6 with an excess of oxidizing agent, and in the absence of zinc oxide or hydroxide, we were able to attain a considerable transference of cobalt to the precipitate.

The data obtained offered the possibility of more accurately determining the role of zinc oxide and manganese dioxide in the process of separation of small quantities of cobalt from solution.

The process of separation of cobalt from solution in this way likely proceeds as a result of the oxidation of bivalent cobalt to the trivalent form. The pH value in the solution is higher than the pH of precipitation of $Co(OH)_3$, and the trivalent cobalt ion which formed was combined with hydroxyl groups, giving $Co(OH)_3$. At high concentrations of cobalt in the solution, $Co(OH)_3$ comes down as a precipitate. At low cobalt concentrations the separation of a precipitate was prevented. In this case it is convenient to use a "carrier" – another precipitate, which will on precipitation also entrain the hydroxide of trivalent cobalt. Manganese dioxide, formed during the process of separation of the cobalt, appears to be the most convenient "carrier" for the separation of cobalt, since a more complete entrainment of trivalent cobalt hydroxide will proceed by formation of a precipitate, and not by its simple presence.

It would be possible also to separate the zinc hydroxide in the solution by addition of a certain quantity of alkali. However, because of localization, on separation of zinc hydroxide, at the boundary of contact of the alkali solution and the investigated solution, simultaneous separation of the precipitate in the total volume of solution may not be assured. The oxidation process of the formation of a precipitate of manganese dioxide proceeds a long time and assures the formation of the precipitate in the entire volume of solution – the condition favoring the most complete entrainment of the hydroxide of trivalent cobalt from solution.

The validity of the assumption that trivalent cobalt hydroxide is precipitated was confirmed by experiments with large cobalt concentrations. On addition of 10 ml of a 0.2 N solution of cobalt to a mixture containing 0.01 g-equiv of zinc hydroxide and 0.01 g-equiv of zinc as a 0.1 N solution of zinc sulfate, cobalt did not precipitate. After boiling such a mixture with an excess of potassium persulfate, a black precipitate formed. The filtered precipitate had oxidizing properties. An iodometric determination indicated the presence in the precipitate of 0.001 g-equiv of oxidizing agent (9.5 $\pm$ 0.3 ml of 0.1 N solution of thiosulfate was consumed in the titration), which corresponded to the presence of trivalent cobalt in the precipitate.

We were unable to obtain a direct indication that during the separation of small quantities of cobalt from the solution, together with manganese dioxide, cobalt was also precipitated in the trivalent form. However, a rather conclusive circumstantial indication was that the separation of cobalt from a solution proceeds only in the presence of an excess of oxidizing agent. While there are still bivalent manganese ions (reducing agent) in the solution, the separation of cobalt does not occur.

SUMMARY

1. A method of separation of small quantities of cobalt from solutions was investigated. A solution of zinc sulfate containing 0.005 g/liter of cobalt was selected as the object of investigation.

2. The inapplicability of the method of cementation for separation of small quantities of cobalt from a solution of zinc sulfate was shown.

3. The feasibility of the joint precipitation of cobalt during the quantitative oxidation of manganese dioxide to the quadrivalent state by the action of potassium permanganate, potassium chlorate and potassium persulfate was investigated.

4. The completeness of the extraction of cobalt was brought to perhaps 0.05 mg/liter and less.

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DIELECTRIC PERMEABILITY OF BINARY LIQUID SYSTEMS CONTAINING ASSOCIATED COMPONENTS

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The determination of the dielectric permeability has been used by a number of investigators for the elucidation of the chemical interaction between components in binary and ternary liquid systems.

Thus, for example, in 1910 D. Dobroserdov [1], studying the dielectric permeability of a series of binary systems, concluded that the main cause of the anomalous relation of the dielectric permeability to the composition (appearance of maxima and minima) was only the chemical interaction between the components in the system.

V. Ya. Krasilnikov, using the Drud method, investigated the dielectric permeability of several binary liquid systems in relation to composition, particularly systems formed by allylic mustard oil and ethyl- and diethylaniline [2]. Important work in this direction was recorded by I. A. Sheka [3, 4]. He developed a method for the determination of the composition of complex compounds in solutions, by the variations of dielectric permeability values, and he recorded an attempt to apply the deviation of the permeability from additive values as a "property" for the purposes of physico-chemical analysis.

A series of investigations in this direction was carried out by Smyth and Engel [5], Errera [6], Earp and Glasstone [7], Altschuller [8], Gritchfield [9] and other authors. All of the works enumerated indicated the applicability of the dielectric permeability as a property for the purposes of physico-chemical analysis.

As is known, the association phenomenon is usually observed for polar molecules; therefore, a study of the dielectric permeability and the dipole moments of liquid systems containing associated components, can shed light on a whole series of still unsolved problems of intermolecular reaction.

It is also necessary to note that establishment of the forms of the isotherms of systems containing chemically non-reacting associated components has paramount value for derivation of the types of isotherms of irrational and rational systems.

In the present work we cited the results of an investigation of the dielectric permeability of the systems, nitrobenzene–isobutyl alcohol, acetone–isobutyl alcohol, and aniline–isobutyl alcohol, at 20°C.

Substances and procedure. The components were purified in the following way. Isobutyl alcohol was dried for a long time over freshly-calcined lime, and then distilled over it. By a second distillation, a fraction boiling at 107.8-108.1° (759 mm): d_4^{20} 0.8019, n_D^{20} 1.3959, was taken for the operation. Nitrobenzene of pure analytical grade quality, after drying over calcined calcium chloride, was distilled at 210.0-210.8° (760 mm): d_4^{20} 1.2027, n_D^{20} 1.5525. Acetone was dried for a long time by potash, distilled, dried once more by calcium chloride, and finally was distilled at 56.3-56.5° (758 mm): d_4^{20} 0.7917, n_D^{20} 1.3592. The aniline was steeped over potassium hydroxide and distilled at 183,5-184° at standard pressure: d_4^{20} 1.0218, n_D^{20} 1.5863.

The composition of the solutions was always expressed in molecular percentages. The dielectric permeability of the solutions was determined by the pulse method at a frequency of 500 kc. The apparatus had two specular coaxial scales; a basic scale from 0 to 105 $\mu\mu F$ with graduation values of 0.5 $\mu\mu F$, and an auxiliary scale from 0 to $\pm$ 0.6 $\mu\mu F$ with graduation values of 0.005 $\mu\mu F$.

The liquid condenser was carefully hermetically sealed off from the environment. The calibration of the vessel (condenser) was made with air, benzene, carbon tetrachloride, acetone and ethyl ether. The substances were carefully purified for the calibration. Determination of the dielectric permeability at 20° was made with an accuracy of $\pm$ 0.1°.

DISCUSSION OF RESULTS

The results of the dielectric permeability determinations of the systems nitrobenzene–isobutyl alcohol (ϵ_I), acetone–isobutyl alcohol (ϵ_{II}), and aniline–isobutyl alcohol (ϵ_{III}) are presented in Fig. 1.

According to the data of Fig. 1, it is evident that for all three systems the dielectric permeability isotherms, in relation to the composition, are curves which are convex toward the composition axis, and the isotherm of the system, acetone–isobutyl alcohol, even has a minimum corresponding almost to an equimolar ratio of the components.

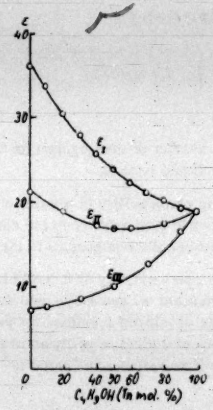

Fig. 1. Dielectric permeability values of systems in relation to the composition. Elucidation in text.

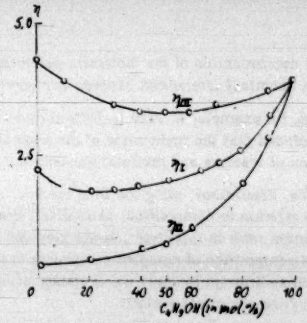

Fig. 2. Viscosity values of the systems in relation to the composition. Elucidation in text.

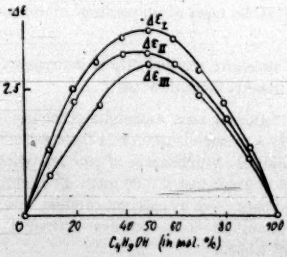

Fig. 3. Deviation of dielectric permeability experimental curves of the systems from the values calculated by the law of additivity. Elucidation in text.

The viscosity isotherms of the systems indicated at 20° are presented in Fig. 2. We measured the viscosity for the systems acetone–isobutyl alcohol (η_{II}) and aniline–isobutyl alcohol (η_{III}), but for the system nitrobenzene–isobutyl alcohol (η_I) we used the data of N. N. Efremov [10], which we converted for 20°. As is apparent from the data of Fig. 2, the viscosity isotherms are similar in form to the dielectric permeability curves, i.e., they are convex toward the concentration axis.

Fig. 3 characterizes the deviations of the dielectric permeability for our systems from the value calculated from the combination rule. From the figure it results that the largest negative deviations of the experimental isotherms from additivity occur in the region close to an equimolar ratio of components, and according to the magnitude of the deviation our systems are arranged as follows:

$$C_6H_5NO_2–C_4H_9OH(\Delta\varepsilon_I) > CH_3COCH_3–C_4H_9OH(\Delta\varepsilon_{II}) > C_6H_5NH_2–C_4H_9OH(\Delta\varepsilon_{III}).$$

It is curious to note that the dipole moment values of the second component decrease in a similar direction.

As is known, in physico-chemical analysis we judge the chemical interaction between components in the system from the form of the "composition-property" curve.

According to the classification of the internal fraction isotherms of the binary liquid systems presented in Fig. 2, the viscosity curves should relate to systems formed from chemically non-interacting, associated components.

The significant convexity of the viscosity isotherms of our systems toward the composition axis indicates a relatively large tendency of the components toward dissociation.

A comparison of the experimental dielectric permeability and viscosity isotherms, as two volumetric properties, showed that they are similar in shape and, consequently, reflect the same process occurring in the system, namely, the decomposition of the associated molecules.

It follows from what has been stated that the dielectric permeability isotherms of binary liquid systems consisting of polar components, can have the form of curves which are convex toward the composition axis.

Errera [6] attempted to find a connection between the viscosity, the vapor pressure and the polarity of the molecules. He concluded that in mixtures consisting of polar and nonpolar liquids, the latter decrease the forces acting between the polar molecules; therefore, the vapor pressure increases and the viscosity decreases.

Thus, the viscosity isotherm of such a system will be convex toward the concentration axis.

According to Errera, the effect should be the reverse for mixtures of two polar substances, i.e., the vapor pressure decreases and the viscosity increases. Consequently, if we hold to the point of view of Errera, then we can conclude that the viscosity isotherms of systems consisting of two polar components should be convex toward the composition axis. However, numerous experimental data occur in contradiction to the point of view stated by Errera [11-13]. As shown by Smyth and Engel [5], mixtures of alcohols with other polar liquids give vapor pressure curves with concavities toward the composition axis side, and they differ little from curves of mixtures of alcohols with nonpolar components.

The viscosity data for the systems which we studied (Fig. 2) also are in contradiction with the conclusions of Errera.

Of course, it is noted that the phenomenon observed by Errera depends not only on the forces acting between 1-2 polar molecules, but also on the forces acting between like molecules, 1—1 and 2—2. In relation to the ratio of these forces the viscosity isotherms can also be convex toward the composition axis, which is often observed.

The statements made also apply to the dielectric permeability isotherms of binary liquid systems containing polar components.

SUMMARY

1. The dielectric permeability of the systems, nitrobenzene—isobutyl alcohol, acetone—isobutyl alcohol, and aniline—isobutyl alcohol were studied.

2. It was found that the dielectric permeability isotherms of all three systems are curves which are convex toward the composition axis.

3. We compared the viscosity and dielectric permeability isotherms of the systems studied, and showed that they are similar to each other in shape and reflect the process of the decomposition of associated molecules.

4. On the basis of our experimental data, the inaccuracy of Errera's views on the behavior of mixtures of two polar components was shown.

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POTENTIOMETRIC STUDY OF Ce (IV) AND Ce (III) PRECIPITATES BY THE EFFECT OF THE pH OF THE SOLUTION ON THE VALUE OF THE OXIDATION-REDUCTION POTENTIAL OF THE SYSTEM Ce^{4+}/Ce^{3+}

T. N. Bondareva and A. G. Stromberg

The oxidation-reduction potential of the system Ce^{4+}/Ce^{3+} was studied by Smith [1]. According to his data, the potential depends on the fact that the cerium salt dissolved in any acid and at any concentration of this acid. The largest value of the potential, 1.87 V was observed in 8 N perchloric acid [1], and the smallest, 1.28 V, was observed for 1 N hydrochloric acid. The potential hardly changes in a sulfuric acid medium with an acidity from 1 to 8 N, and is equal to 1.44 V on the average.

The potential of the system Ce^{4+}/Ce^{3+} in slightly acid, neutral and alkaline solutions was studied by one of us [2], but in that work we obtained only a few points on the curve relating the potential to the pH of the solution, which did not enable us to arrive at definite physico-chemical results.

The purpose of the present work was a more detailed study of the relation of the potential of the system Ce^{4+}/Ce^{3+} to the pH of the solution in slightly acid and alkaline solutions, the elucidation of this relationship in connection with the deposition of precipitates of the hydroxides of quadri- and trivalent cerium, and also an approximate determination of the solubility products of the hydroxides which formed.

The measurement of the potential was made by a method described in the literature [3]. For measurement of the potential, we used a potentiometer of the PPTV-1 system. A galvanometer with a sensitivity of $6.7 \cdot 10^{-8}$ amp served as the null instrument. We used a mercuric sulfate-mercurous oxide electrode as the reference electrode.

About 50 ml of 0.02 N solutions of tri- and quadrivalent cerium were poured into a 1 N solution of sulfuric acid (total volume of solution 100 ml) in the vessel for measurement of the potential.

A 10 N solution of NaOH was placed in a burette. The first measurement of the potential was made without addition of alkali, i.e., in 1 N H_2SO_4, after which we gradually ran alkali into the vessel. After each addition of alkali, the solution was agitated by passing through a current of oxygen-free nitrogen, until the potential acquired a constant value. As a rule, the potential reached a constant value after 1-2 minutes. The pH of the solution was measured with a glass electrode made from "Corning 0.15 glass."

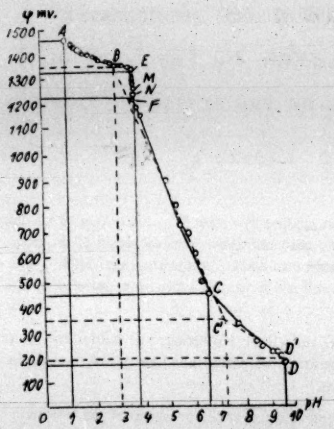
The relation of the potential of the system to the acidity of the medium was determined at pH ranges from 1 to 9.55. When the pH of the solution reached a value of 2.73, the 10 N alkali was replaced by 2 N alkali. This replacement was made in order to detect a change of potential of the system in the region close to neutrality. After attainment of a pH of 8.5, we again used the 10 N alkali. All the measurements were made at 25°.

Under the conditions described above, we repeated the potentiometric titrations with a solution of alkali several times, with good reproducibility. The results of one of the experiments are presented in the table.

On the basis of the data cited in the table, a curve relating the oxidation-reduction potential of the system Ce^{4+}/Ce^{3+} to the pH of the solution (figure) was plotted.

According to its nature, the curve could be broken into four sections, AE, EF, FC and CD.

The first section of the curve, AE, within the pH limits from 1 to 3.75, is characterized by a slow decrease of the potential from 1.46 to 1.33 V; moreover, a gradual decolorization of the solution was observed. In the second section of the curve, EF, a change of potential of the system from 1.33 to 1.23 V took place at a constant pH of 3.75. At point M the solution opalesced noticeably. At point N a white precipitate deposited. In the third section, FC, by variation of the pH from 3.75 to 6.55, the potential decreased from 1.23 to 0.44 V, whereby the points satisfactorily fell on a straight line. At a pH of 5.3, the precipitate acquired a cinnamon tint, which intensified in proportion to the pH increase. The fourth section was characterized by a further decrease of the potential, but more slowly than for the third section. The relation of the potential to the pH in this section was also expressed by a straight line on the graph.



Relation of oxidation-reduction potential of system Ce^{4+}/Ce^{3+} to pH of the solution.

If for simplicity of explanation, section BEF is not considered at first, but through the points of sections FC and CD straight lines are drawn until they intersect, then we obtain two straight lines BC' and C'D', which have different angular coefficients.

The following chemical reactions can take place in the system:

$$H_2SO_4 + 2OH^- \rightleftharpoons SO_4^{2-} + 2H_2O, \quad (1)$$

$$[Ce(SO_4)_3]^{2-} + 2OH^- \rightleftharpoons (Ce^{4+} + 3SO_4^{2-} + 2OH^-) \rightleftharpoons$$

$$\rightleftharpoons CeO^{2+} + 3SO_4^{2-} + H_2O, \quad (2)$$

$$CeO^{2+} + 2OH^- \rightleftharpoons CeO(OH)_2, \quad (3)$$

$$Ce^{3+} + 3OH^- \rightleftharpoons Ce(OH)_3. \quad (4)$$

In section AB there was no precipitate. Two reactions are possible here: Reaction (1) of the neutralization of sulfuric acid, and Reaction (2), of the interaction of the complex ion $[Ce(SO_4)_3]^{2-}$ with hydroxyl ions, as a result of which CeO^{2+} ions are formed.

The oxidation-reduction potential of the system Ce^{4+}/Ce^{3+} depends on the activities of the ions of tri- and quadrivalent cerium.

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \frac{a_{Ce^{4+}}}{a_{Ce^{3+}}}, \quad (5)$$

or

$$\varphi = \varphi^0 + \frac{RT}{F} \ln \frac{c_{Ce^{4+}} \cdot f_{Ce^{4+}}}{c_{Ce^{3+}} \cdot f_{Ce^{3+}}}. \quad (6)$$

TABLE

Relation of Oxidation-Reduction Potential of the System Ce^{4+}/Ce^{3+} to the pH of the Solution

pH of solution	φ, with reference to the S.H.E.* (in mV)	pH of solution	φ, with reference to the S.H.E. (in mV)	pH of solution	φ, with reference to the S.H.E. (in mV)
1.00	1460	3.38	1350	4.20	1079
1.30	1440	3.60	1347	4.90	898
1.40	1429	3.65	1344	5.30	797
1.52	1423	3.70	1337	5.50	717
1.58	1420	3.75	1328	5.75	686
1.60	1416	3.75	1316	6.10	607
1.70	1410	3.75	1311	6.35	492
1.95	1401	3.75	1296	6.55	442
2.15	1389	3.75	1290	7.70	322
2.26	1381	3.75	1269	8.40	266
2.30	1377	3.75	1259	8.65	224
2.73	1368	3.75	1246	9.12	217
2.90	1360	3.75	1228	9.20	210
3.05	1357	3.90	1187	9.40	191
3.20	1355	4.00	1154	9.55	163

On dilution of the solution, due to the increase of the volume of alkali added, the concentrations of the tri- and quadrivalent cerium ions decreased to the same extent, so the concentration ratio would remain a constant value. The ratio of the activity coefficients of tri- and quadrivalent cerium ions also changed little, since in this section the ionic strength of the solution hardly changed. Consequently, as is evident from Formula (6), the potential of

* S.H.E. equals Standard hydrogen electrode.

the system would probably remain almost constant. However, we observed an appreciable decrease of the potential; moreover, a decolorization of the solution occurred. This can be explained as follows.

On addition of the alkali, a destruction of the colored (orange) complex $[Ce(SO_4)_3]^{2-}$ occurs according to reaction 2, with the formation of CeO^{2+} ions.

We cite some calculations in confirmation of the assumption stated.

The activity of the Ce^{4+} ions can be determined from the expression for the equilibrium constant of Reaction (2):

$$K_c = \frac{a_{CeO^{2+}}}{a_{Ce^{4+}} \cdot a^2_{OH^-}}. \quad (7)$$

Substituting the value $a_{Ce^{2+}}$ from Equation (7) into Equation (5), we obtain:

$$\varphi = \varphi^0 + 0.059 \log \frac{a_{CeO^{2+}}}{K_c \cdot a_{Ce^{3+}}} + 1.65 - 0.118\ pH. \quad (8)$$

For a constant value of $a_{CeO^{2+}}$ the relation of φ to the pH should be expressed by a straight line with an angular coefficient of 0.118. However, on addition of the alkali $a_{CeO^{2+}}$ increased, and this led to the fact that the potential decreased not so sharply, as it did for a constant $a_{CeO^{2+}}$.

Further neutralization of the sulfuric acid, and the separation of a precipitate of quadrivalent cerium proceeds in section BC'; moreover, at first the precipitate is white. On further addition of alkali, the precipitate becomes cinnamon-colored.

According to literature data, the hydroxide of quadrivalent cerium $Ce(OH)_4$ has a cinnamon color. It may be assumed that the white precipitate corresponds to the formula $CeO(OH)_2$. It forms as a result of reaction (3). For verification of this assumption, we should calculate the angular coefficient of line BC' and compare the value obtained with that found practically.

The activity product of the $CeO(OH)_2$ precipitate is:

$$L_{a\,CeO(OH)_2} = a_{CeO^{2+}} \cdot a^2_{OH^-}. \quad (9)$$

Because the activity coefficient of the CeO^{2+} ion is unknown, we will make a further approximate calculation by the use of the ionic concentrations:

$$L_{c\,CeO(OH)_2} = c_{CeO^{2+}} \cdot c^2_{OH^-}. \quad (10)$$

It can be assumed that at point B of the curve in the figure, practically all of the quadrivalent cerium occurs as CeO^{2+} ions, since in connection with the increase of the hydroxyl ion concentration in the solution, the equilibrium according to Equation (2) should be shifted toward the right. From the literature [1] it is known that the complex of cerium with sulfate-ion is orange-colored. On approaching point B, we observed a decolorization of the solution, which indicated the practically complete dissociation of this complex according to Equation (2).

Calculating the concentration of quadrivalent cerium by calculation of the volume of alkali added, and determining the hydroxide ion concentration from the pH values of the solution observed, we found $L_{c\,CeO(OH)_2} \simeq 10^{-26}$.

For calculation of the angular coefficient of line BC', we determined the activity of Ce^{4+} ions from equation (7) and the activity of CeO^{2+} ions from Equation (9), and substituted the resulting expressions into Formula (5):

$$\varphi = \varphi^0 + 0.059 \log \frac{L_{a\,CeO(OH)_2}}{K_c \cdot a_{Ce^{3+}}} + 3.30 - 0.236\ pH. \quad (11)$$

Hence, the angular coefficient of the line in the φ and pH coordinates equals $\frac{d\varphi}{dpH} = -0.236 = \text{const}$, since the activity of the Ce^{3+} ions in this section remains constant. Consequently, in all fairness to the assumptions made above, the relation of φ to pH should be expressed by a straight line with an angular coefficient of -0.236. From the experimental data (see figure), the value of the angular coefficient of line BC' is -0.24. This experimental value of the angular coefficient agrees well with its theoretical value, -0.236.

The appearance of a cinnamon-colored precipitate at a pH of 5.3 may be explained by the reaction:

$$CeO(OH)_2 + H_2O = Ce(OH)_4. \quad (12)$$

Since OH^- ions do not participate in this reaction, the angular coefficient remains unchanged.

Reactions (12) and (4) take place in section C'D'. At point C' a precipitate of the hydroxide of trivalent cerium begins to separate. Its activity product is:

$$L_{aCe(OH)_3} = a_{Ce^{3+}} \cdot a^3_{OH^-}. \quad (13)$$

The value L_a of the $Ce(OH)_3$ precipitate can be calculated by determining the concentration of Ce^{3+} ions from the total concentration of the trivalent cerium salt, by calculation of the dilution of the solution due to the volume of alkali added, and determining the hydroxyl ion concentration from the pH value.

The approximate value of the solubility product calculated in this way was $L_{a\,Ce(OH)_3} \simeq 10^{-23}$.

In order to calculate the angular coefficient of line C'D', we determined the activity of the trivalent cerium ions from Equation (13) and the activity of the quadrivalent cerium ions from the equation:

$$L_{aCe(OH)_4} = a_{Ce^{4+}} \cdot a^4_{OH^-}. \quad (14)$$

Substituting these activity values into Equation (5), we obtain:

$$\varphi = \varphi^0 + 0.059 \log \frac{L_{a\,Ce(OH)_4}}{L_{aCe(OH)_3}} + 0.83 - 0.059\ pH. \quad (15)$$

Hence, the angular coefficient of line C'D' on the φ and pH coordinates equals $\frac{d\varphi}{dpH} = -0.059 = \text{const.}$

Consequently, in this case, in all fairness to the assumption made above, the relation of the potential to the pH of the solution should be expressed by a straight line with an angular coefficient equal to -0.059. From the graph we find the usual value of the angular coefficients of the straight line to be -0.064, which agrees satisfactorily with the theoretical.

Thus, the linear form of segments BC' and C'D' on the graph with φ and pH coordinates, and the angular coefficients of these lines, confirmed the assumption stated concerning the composition of the precipitates which separated.

At present we find it difficult to give and accurate explanation of section BEF on line BC'. It can be assumed that in section BEF of the curve, we have a supersaturated solution of $CeO(OH)_2$, because of the absence in solution of crystals of solid phase above the critical size.

The supersaturation phenomenon was not observed at point C', since solid phase $Ce(OH)_4$ is present in the solution, and may serve as the center of crystallization for a new phase.

Thus, the potentiometric study of the relation of the oxidation-reduction potential of the system Ce^{4+}/Ce^{3+} to the pH of the solution enabled us to obtain a series of interesting data on the order of separation of hydroxide precipitates of ions of different valences, and some data on their composition and on the solubility products of these precipitates. A complete judgment of the composition of the precipitates which separated, would require a chemical analysis of these precipitates, which did not enter into the problem of the present work.

SUMMARY

1. The relation of the potential of the system Ce^{4+}/Ce^{3+} to the pH of the solution was studied in a pH range from 1 to 9.5.

2. A theoretical interpretation of the relation obtained was given. The linear section BC' on the graph, with an angular coefficient of 0.24, was related to the separation of the Ce (IV) hydroxide of composition $CeO(OH)_2$, and later $Ce(OH)_4$. On the graph, the linear section with an angular coefficient of 0.06, was related to the simultaneous separation of Ce (IV) and Ce(III) hydroxides of compositions $Ce(OH)_4$ and $Ce(OH)_3$.

3. The approximate values of the solubility products of the Ce (III) and Ce (IV) hydroxides were calculated.

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PREPARATION AND INVESTIGATION OF THE CITRATE COMPLEX OF COBALT

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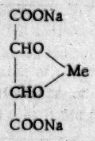
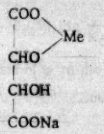
It was shown by the investigation of tartrate complexes [1] that, depending on the quantitative proportions of the components of the system – tartrate, alkali and metal salt – three types of complexes form:



(I)



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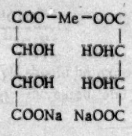


(III)

We wanted to convince ourselves of the feasibility of the preparation of such complexes with salts of citric acid, since it was assumed that the character of the complex formation observed in a system with tartrates applies to the salts of hydroxylacids in general.

Different alkali solutions of sodium citrate were prepared (Table 1) for the preparation and study of the citrate complexes of cobalt.

TABLE 1

Sodium nitrate solutions	0.5 N solution of $Na_3C_6H_5O_7$ (ml)	0.5 N solution of NaOH (ml)	Proportion of equivalents	
			$Na_3C_6H_5O_7$	NaOH
1	90	10	10	1
2	88.8	11.2	8	1
3	87.5	12.5	7	1
4	85.8	14.3	6	1
5	80.0	20.0	4	1
6	75.0	25.0	3	1
7	66.6	33.3	2	1
8	100	–	–	–
9	100*	–	–	–

The complex indicated in Table 1 was partially decomposed by an increase of the alkali concentration in solution. This can be judged by the appearance of an insoluble precipitate on addition of a cobalt salt. It amounts to observing the following fact: the precipitate of $Co(OH)_2$ which formed gradually turned brown, i.e., was converted to $Co(OH)_3$, dissolved after several days, and the entire solution acquired a brick-red color.

The method of investigation of the stability of the complex by titration of the alkaline solution of a citrate metal salt and vice versa [1] is also inadmissible in the present case because the reaction proceeds imperceptibly. By the qualitative reactions for determining the presence of Co^{++} ions we studied the stability of the complex which formed in the solutions (Table 2), obtained by the addition of 5 ml of 0.5 N solution of $CoCl_2$ to 20 ml of alkaline citrate solutions, specified in Table 1. The complex was unstable upon increase of the quantity of cobalt salt of the solution (above a 1:4 ratio).

The Co^{++} ion was not detected in any of the solutions by the Na_2CO_3 reagent.

* Solution No. 9 during preparation was neutralized with acid in the presence of methyl orange indicator.

TABLE 2

Solutions of complexes	Reagents			
	Na_2S	$(NH_4)_2S$	KCNS	$K_4[Fe(CN)_6]$
1	+	+	−	+
2	+	+	−	+
3	+	+	−	+
4	−	−	−	−
5	−	−	−	−
6	−	−	−	−
7	+	+	−	−
8	+	+	−	+
9	+	+	+	+

Note: 1) A plus (+) sign denotes the presence of Co^{++} ions in the solution; a minus (−) sign denotes their absence. 2) At the moment of preparation of the solutions (in a period of 1 hour) Co^{++} ions were observed in all the solutions by means of Na_2S and $(NH_4)_2S$; in Table 2 are data obtained 2 hours after preparation of the solutions.

The results obtained for the individual reactions were confirmed after 24-48 hours, except for Solution No. 4, in which after 24 hours a slight turbidity appeared on addition of Na_2S or $(NH_4)_2S$.

The data of Table 2 convinced us of the following:

1. The stability of the complex is most expressed in the presence of Solutions Nos. 4, 5 and 6, i.e., with a 6:1-3:1 ratio of equivalents of sodium citrate and alkali.

For the purposes of analysis, under the conditions indicated, the cobalt in the solutions could be masked.

2. The $[Fe(CN)_6]^{4-}$ ion does not give a characteristic reaction with cobalt. On addition of $K_4[Fe(CN)_6]$ to Solution No. 3 a turbidity formed, but in Solutions Nos. 1, 2 and 8 a light, flesh-colored precipitate formed, and in Solution No. 9 a yellowish-colored precipitate formed.

3. In the presence of sodium citrate (Solution No. 9) at a pH of 3.1-4.4 the stability of the complex is less (judging by the action of KCNS), compared to a solution of $Na_3C_6H_6O_7$ at a pH of 7-7.5 (Solution No. 8); this indicates the rupture of the ring in an acid medium [2].

This information provides the initial requirements for the determination of the composition of the complexes. Knowing from our previous investigations that complexes of types I or II are obtained only in the presence of alkaline solutions of salts of hydroxy acids, and by means of only one salt of a hydroxy acid of complex III type, we carried out the determination of the composition under suitable conditions.

For the precipitation of tartrate complexes, in the determination of the composition, we added ethyl alcohol. Ethyl alcohol, as we found, did not precipitate the cobalt citrate complexes.

We developed the following method for the determination of their composition.

1. Into 20 ml of a sodium citrate solution we poured 5 ml of a 0.5 N solution of $CoCl_2$. For precipitation, after two hours we poured in 100 ml of CH_3OH and allowed the resulting turbid solution to stand for 3 hours. Then the filtrate was poured off, and the precipitate, which separated as a rose-red "scum", was washed by decantation (until the removal of Cl^-) with methyl alcohol. On washing with alcohol the precipitate became viscous, and then gradually crystallized. The beaker and precipitate were dried at 105-120°.* A weighed portion of 0.11-0.24 g was charred in a platinum crucible on the electric plate, and then was calcined in a crucible furnace. After calcination, the residue was transferred to a beaker, treated with hot water, warmed up and allowed to stand. After this the solution was carefully filtered off (through a double filter) into a flask. This operation was carried out until the solution no longer became neutral to phenolphthalein. After washing the precipitate from the beaker, it was transferred to a filter. The quantity of alkali in the filtrate was determined and listed as sodium.

The filter and precipitate were transferred to a platinum crucible, burned and calcined; then H_2SO_4 was added and it was carefully warmed up in a large porcelain crucible until the removal of SO_3. If the precipitate (as black granules) did not dissolve completely, then several drops of concentrated HNO_3 were added and the precipitate was warmed up, and the operation repeated with H_2SO_4 until complete removal of SO_3. Cobalt was determined as $CoSO_4$ [3]. Such a determination of cobalt was a laborious operation; nevertheless, losses were inevitable if the conditions indicated were not observed.

2. The determination of the composition of the complex which formed on reaction of sodium citrate solutions (without alkali) and a cobalt salt was essentially analogous to that described above, with this difference, that the solution should stand for 12 hours after addition of methyl alcohol for precipitation. Then the filtrate was poured off and the precipitate was washed with dilute methyl alcohol (1 part of alcohol + 2 parts of water) until the removal of

* The precipitation was repeated several times for preparation of an adequate quantity of complex salt.

Cl^-. The precipitate was dried at 105-120° and analyzed.

The dry precipitate from Solution No. 4 was rose-red and crystalline; on dissolving in water it gave no precipitate with Na_2S. The reaction of the solution was alkaline toward phenolphthalein.

Analysis of the dry precipitate from Solution No. 4

0.1176, 0.1872, 0.1328* g sub.; 8.1, 12.8, 9.2 ml 0.1 N HCl; 0.0634, 0.0964, 0.0738 g $CoSO_4$. Found %: Na 15.84, 15.72, 15.32; Co 20.50, 19.60, 20.28. $Na_3[CoC_2H_2O_7]$. Calculated %: Na 15.70; Co 20.12.

The dry precipitate from Solution No. 8 had a flesh-rose color and was crystalline; it was insoluble in water. The reaction of the solution toward phenolphthalein was neutral.

Analysis of the dry precipitate from Solution No. 8

0.2184, 0.2320 g sub.; 16.2, 17.6 ml 0.1 N HCl; 0.0610, 0.0676 g $CoSO_4$. Found %: Na 17.70, 17.45; Co 11.02, 11.97. $Na_4[Co(C_2H_2O_7)_2]$. Calculated %: Na 17.39; Co 11.14.

DISCUSSION OF RESULTS

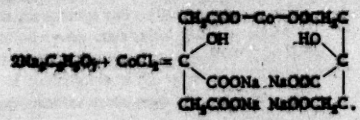
As was found [1], complex formation takes place in the presence of a mixed peptide* (a mixture of a tartrate solution and an alkali solution) because of the hydroxyl groups or because of one hydroxyl and carboxyl group of the tartrate. The preparation of the compound due only to the tartrate carboxyl groups proceeds with participation of only the tartrate salt (without alkali).

In the presence of an alkaline citrate solution with equivalent ratios of citrate and alkali in the range 4:1-8:1, in the case described, the formation of the complex proceeds due to the hydroxyl and carboxyl groups.

$$Na_3C_2H_2O_7 + OH^- \rightleftarrows Na_2C_2H_2O_7^- + NaO$$

$$Na_2C_2H_2O_7^- + Co^{++} = Na_2[CoC_2H_2O_7] + Na^+ .$$

With the participation of the sodium citrate solution the production of a compound takes place only due to the citrate carboxyl groups.



Consequently, in the main, the formation of cobalt tartrate and citrate complexes occurs identically.

SUMMARY

1. The complex $Na_3[CoC_2H_2O_7]$ formed on addition of an excess of an alkaline solution of sodium citrate, with equivalent ratios of $Na_3C_2H_2O_7$ and NaOH of 4:1-8:1, to a cobalt salt. This complex is so stable that the cobalt ion is not detected in the solution by the usual reagents.

2. The complex $Na_4[Co(C_2H_2O_7)_2]$ was obtained by reaction of sodium citrate solutions and a cobalt salt with equivalent ratios of 4:1.

3. A method was developed for the preparation and determination of the composition of the complexes.

4. In the present example the point of view of the chemism of the reaction of complex formation by the participation of the salts of hydroxy acids was confirmed.

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Kiev Hydro-Development Institute

* Batch of the material from Solution No. 4: alkaline citrate solution 24 ml, cobalt salt 4 ml.

A MASS-SPECTROMETRIC INVESTIGATION OF THE ORGANOCHLOROSILANES

N. N. Sokolov, K. A. Andrianov and S. M. Akimova

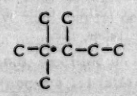
The analysis of different substances by means of a mass-spectrometer is one of the new and useful methods of studying different compounds. Mass-spectrograms offer the possibility of making deductions concerning the formulas of substances, concerning the composition of mixtures of different substances, etc.. Mass-spectrometry has received special development in application to the analysis of mixtures of aliphatic hydrocarbons (review articles [1, 2]).

Mass-spectrometric investigations still have been little used in applications to organosilicon compounds, which in the past decade have received much development in theoretical and practical respects [3]; in the literature only brief notes have been published concerning the analytical application of mass-spectrometry to this field [4, 5], and also concerning the ionization mechanism of tetramethylsilane [6], hexamethyldisiloxane and octamethyltrisiloxane [7].

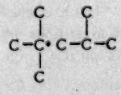
The study of the mass-spectrogram of an important class of organosilicon compounds – the organochlorosilanes – seemed to be of primary importance in the present investigation. The organochlorosilanes serve as one of the chief sources of the production of high-molecular organosilicon products [3, 8]. Organochlorosilanes of the general formula R_nSiCl_{4-n}, where $n = 1-3$, and R is the methyl, ethyl or phenyl radical, were used for the experiments.

First of all, the obtaining, of a mass-spectrogram of the organochlorosilanes is of interest in an analytical respect. In the ionization chamber of the mass-spectrometer molecules either do not undergo decomposition, and are only ionized, acquiring a positive charge, or they decompose to individual, positively charged, and correspondingly neutral particles (fragments) with the loss of an electron. The mass-spectrograms obtained showed that the organochlorosilanes give decomposition product complexes of the molecules which are characteristic of each given compound. For definite parameters and method of work, with the mass-spectrometer a definite composition of particles, which are identified by the mass value (quality) and by the peak value for the given mass (quantity), is obtained. In analytical work the quantity of each substance in a mixture is determined by calculation of the total peak values in the presence of coincidence of the masses [9]. We should also have in mind that for each given design of mass-spectrometer, discrepancies in the peak values are obtained, which however, do not bear a principle character [10].

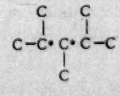
From the theoretical point of view, it was of interest to investigate some of the mechanisms of decomposition of the organochlorosilane molecules in the mass-spectrometer chamber. Until now the mechanism of the ionization process and the decomposition of the molecules had been inadequately studied. Ionization arises when an electron passes sufficiently close to a molecule, so that as a result of the interaction of their fields, the neutral molecule absorbs some energy from the ionizing electron. After this the molecule loses one of its electrons, acquiring a positive charge, or giving up an electron, additionally decomposes into independent particles. In the latter case a positive ion, a neutral particle and an electron form. The relative number of ions of different masses, which form as a result of electronic bombardment, depends on the relative probability of the ionization processes for given types of molecules. Thus, for 2,2,3-trimethylpentane and 2,2,4-trimethylpentane decomposition proceeds such that, for the most part, the molecule divides into two approximately equal parts, each of which contains 4 carbon atoms [11]. The latter is not possible for 2,3,4-trimethylpentane, and decomposition proceeds with the formation of three particles, which contain 3, 3, and 2 carbon atoms, respectively:



2,2,3-Trimethylpentane



2,2,4-Trimethylpentane



2,3,4-Trimethylpentane

The decomposition of compounds with one carbon atom, for example of the methane type, proceeds according to another principle – by means of the subsequent breaking away of hydrogen atoms [12]; adopting CH_4^+ as 100%, we have: CH_3^+ 80.1%, CH_2^+ 8.28%, CH^+ 2.90% and C^+ 0.47%. The same phenomenon is observed for carbon tetrachloride [2].

As shown by our experiments (Tables 5-12), the general scheme of decomposition of the organochlorosilane molecules is represented as follows: by means of the successive breaking away of radicals or chlorine from the molecule, there remain any possible ionized atoms or particles; moreover, as a rule, the particles which separate are, therefore, chlorine isotopes, in case of its presence.

For example, the decomposition of methyltrichlorosilane CH_3SiCl_3 might be represented by the following scheme (the points of decomposition are designated by asterisks):

$RSiCl_3^+$	$R^* SiCl_2^+$
$RSiCl^+ + Cl_2$	$R^* SiCl^+ + Cl_2$
$RSiCl^+ + Cl^* Cl$	$R^* SiCl^+ + Cl^* Cl$
$RSi^+ + Cl^* Cl^* Cl$	$R^* Si^+ + Cl^* Cl^* Cl$
$R^+ + Si^* Cl^* Cl^* Cl$	$R^* + Si^* Cl^+ + Cl^* Cl$

The ionization of the entire initial molecule ($RSiCl_3^+$) with the breaking away of one electron is observed for all types of molecules, besides trimethylchlorosilane.

The decomposition of the molecules is accompanied by decomposition of the organic radicals, whereby the breaking away of hydrogen atoms proceeds with greater difficulty the less hydrogen remains in the particle. For example, for methyl, according to the number of particles, the following regularity is observed (Table 1):

$$CH_3^+ > CH_2^+ > CH^+ > C^+.$$

This regularity agrees completely with the scheme of decomposition of methane [12] and tetramethylsilane [6]. In general, in the majority of cases the radical is preserved in the whole form, probably due to the large value of the C–H bond energy (85.5 kcal). The presence of a partially decomposed radical is also observed in complex particles. Such, for example, is the CH_3SiCl^+ particle in methyltrichlorosilane or ethyltrichlorosilane; triethylchlorosilane gives a spectrum especially rich in such particles as: $(CH_3)_2SiCl^+$, $(CH_3)_3SiCl^+$, $(C_2H_5)CH_3SiCl^+$, $(C_2H_5)(CH_3)_2SiCl^+$, etc..

TABLE 1

Mass	Particle	Content (in %)					
		CH_3SiCl_3	$(CH_3)_2SiCl_2$	$(CH_3)_3SiCl$	$C_2H_5SiCl_3$	$(C_2H_5)_2SiCl_2$	$(C_2H_5)_3SiCl$
13	CH^+	0.73	0	1.08	0	0	0
14	CH_2^+	2.00	1.72	2.25	0.47	0.84	0.24
15	CH_3^+	3.75	4.51	4.50	0.71	1.49	0.61

The decomposition of phenyl, in the case of phenyltrichlorosilane, gives particles of 77, 76, 74, 65, 63, 52, 50, 39, etc., which are characteristic of the decomposition of benzene. The number of Cl^{35+}, as a result of the decomposition was approximately 2-3 times greater than the number of Cl^{37+}, as should be expected from the proportion of these isotopes in chlorine. If the same regularity is also observed for chlorine-containing organic particles (for example, in the decomposition of carbon tetrachloride [12]), then in the decomposition of organosilicon substances, in some cases, the number of particles with the Cl^{37} isotope is larger than with the Cl^{35} isotope. This is observed especially clearly in the presence of two or three chlorine atoms. In order to define this phenomenon more accurately we undertook a mass-spectrometric analysis of silicon tetrachloride. As is evident from the analytical data, the number of ionized particles with the Cl^{37} isotope is clearly greater in the case of retention in the particle of two, three, and four chlorine atoms.

The abundance of recombinations of the decomposing particles is the next distinguishing characteristic of the decomposition of the organosilicon compounds. Thus, there is the recombination of chlorine atoms to Cl_2^{37+} in the case of the methylchlorosilanes. There is this same recombination for $SiCl_4$, in contrast to CCl_4. The recombination of SiH^+ (triethylchlorosilane and phenyltrichlorosilane) is possible. In triethylchlorosilane there are recombinations of $SiCl_2^{35+}$ and $SiCl_2^{37+}$. The recombination of CH_2^+ is observed in methylchlorosilanes, etc..

Recombination is also possible along the line of R–R and R–Cl. For example, $CH_3CH_3^+$ in methylchlorosilanes, $C_6H_5CH_3^+$ and $C_6H_5C_6H_5^+$ in methylphenyldichlorosilane, CH_3Cl^+ in methylchlorosilanes, $C_6H_5Cl^+$, in phenyltrichlorosilane, etc.. Recombinations of such a range are not usually encountered in organic substances.

Let us take up the question of the most probable decomposition, first of all, by formation of ions in the decomposition products available in the greatest number for a given chlorosilane (Table 2).

It follows from the data of Table 2 that decomposition proceeds chiefly, not by means of the division of the molecule into two approximately equal parts (which is also strictly impossible in the present case), but by means of the breaking away of the component which predominates in quantitative relation to the silicon – the organic radical or chlorine. Thus, in the trichlorosilanes, the chlorine atom is broken away first of all, but in the trimethylsilanes the methyl radical is broken away first. In the dialkylchlorosilanes methyl, and not chlorine, breaks away, which evidently is explained by the greater stability of the Si–Cl bond (85.8 kcal) than the Si–C bond (57.6 kcal).

In Table 3 is given the approximate calculation of the percent of rupture of the Si–C and the Si–R bonds from the total mass-spectrogram of each given compound.

TABLE 2

Substance	Particle	Content (%)	Nature of decomposition
Methyltrichlorosilane	$CH_3SiCl_2^+$	13.75	$RSiCl_2^+ + Cl$
Ethyltrichlorosilane	$C_2H_5SiCl_2^+$	17.93	$RSiCl_2^+ + Cl$
Dimethyldichlorosilane	$CH_3SiCl_2^+$	23.20	$R^{\bullet}$ $RSiCl_2^+$
Diethyldichlorosilane	$C_2H_5SiCl_2^+$	11.26	$R^{\bullet}$ $RSiCl_2^+$
Trimethylchlorosilane	$(CH_3)_2SiCl^+$	13.55	$R^{\bullet}$ R_2SiCl^+
Triethylchlorosilane	$(C_2H_5)_2SiCl^+$	9.78	$R^{\bullet}$ R_2SiCl^+

TABLE 3

Substance	Cl:R	Percent of rupture		Si–Cl / Si–R rupture (on the average)
		Si–Cl	Si–R	
Methyltrichlorosilane	3:1	74	42	2:1
Ethyltrichlorosilane	3:1	68	39	
Phenyltrichlorosilane	3:1	57	19	
Dimethyldichlorosilane	2:2	30	73	1:2
Diethyldichlorosilane	2:2	41	70	
Methylphenyldichlorosilane	2:2	45	69	
Trimethylchlorosilane	1:3	24	80	1:3
Triethylchlorosilane	1:3	18	72	

This calculation confirms the conclusion indicated. In compounds of the $RSiCl_3$ type the probability of rupture of the Si–Cl bond is 2 times greater than of the Si–R bond; on the contrary, in compounds of the R_3SiCl type the rupture of the Si–R bond is of greater probability; moreover, the probability of rupture of the Si–R bond decreases with enlargement of the radical. In compounds of the R_2SiCl_2 type the probability of rupture of the Si–R bond is 2 times greater than of the Si–Cl bond.

EXPERIMENTAL

The experimental part was carried out with an A. A. Sakovich design mass-spectrometer. The experiments were made for $U_{electromagnetic}$ 100 V, $I_{electromagnetic}$ 3 mA and $I_{ioniz.}$ 0.01 mA.

The substances to be investigated were collected in a quantity of about 0.5 g in an evacuated glass ampoule, which was then sealed up. The ampoule was placed in a test tube with a ground-glass stopper. The test tube, through a stopcock, was in communication with the mass-spectrometer system. On insertion of the ampoule into the test tube, the drawn-out end of the ampoule was broken off, the stopcock was opened a little and air, together with a small amount of the vapors of the substance to be studied, was removed from the test tube. Then the stopcock was closed, and the mass-spectrometer system was carefully evacuated. After this the stopcock from the test tube was opened again, vapors of the substance to be studied filled a glass cylinder, and were led from the cylinder into the mass-spectrometer chamber. All the experiments were carried out at room temperature.

Organochlorosilanes and silicon tetrachloride with the following properties (Table 4) were used for the experiments.

The number of particles obtained as a result of the decomposition of the organochlorosilanes increased significantly because of the presence of isotopes of chlorine, silicon, carbon and hydrogen.

TABLE 4

Substance	Formula	Molecular weight	Boiling point	Per cent of chlorine	
				calculated	found
Methyltrichlorosilane	$(CH_3)SiCl_3$	149.5	65°	71.18	71.00
Dimethyldichlorosilane	$(CH_3)_2SiCl_2$	129.0	70	54.97	55.08
Trimethylchlorosilane	$(CH_3)_3SiCl$	108.6	57	32.64	33.10
Ethyltrichlorosilane	$(C_2H_5)SiCl_3$	163.5	99	65.08	64.97
Diethyldichlorosilane	$(C_2H_5)_2SiCl_2$	157.1	129	45.16	45.00
Triethylchlorosilane	$(C_2H_5)_3SiCl$	150.5	143	23.55	23.52
Phenyltrichlorosilane	$(C_6H_5)SiCl_3$	211.4	200	50.31	50.20
Methylphenyldichlorosilane	$(CH_3C_6H_5)SiCl_2$	191	203	37.17	37.28
Silicon tetrachloride	$SiCl_4$	169.9	56	83.49	83.45

The chlorine isotopes exist in entirely proportionate quantities [13, 14]: Cl^{35} 75.43%, Cl^{37} 24.57%. The chlorine isotopes were also clearly indicated on the mass-spectrograms. We also observed particles with mixed chlorine isotopes, for example $CH_3SiCl^{37}Cl_2^{35}$. However, the majority of particles did not have mixed isotopes, and therefore, for the purposes of abridgment of the tables, the particles with mixed chlorine isotopes are not cited below.

The silicon isotopes were as follows: Si^{28} 92.16%, Si^{29} 4.71% and Si^{30} 3.13%. The carbon isotopes were: C^{12} 98.9%, C^{13} 1.1%. The hydrogen isotopes were: H^1 99.984%, H^2 0.016%. Because of the small content of the rare isotopes and the great difficulties of interpretation, we considered only the principal isotopes of Si, C and H.

The difficulties, which the interpretation of the mass values of the resulting particles present are well-known. In a number of cases there is the possibility of different interpretations of the mass obtained, for example: mass 28 – Si, CH_3CH, traces of nitrogen; mass 52 – C_4H_4 or CH_3Cl^{37}, etc.; therefore, we should keep in mind that in the decomposition tables some of the formulas for the particles are of a hypothetical nature, and some of the masses have not been altogether deciphered. For purposes of abridgment of the tables, the particles with masses up to 28 are not given; calculation of the percentages were made with their consideration.

TABLE 5

Methyltrichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	5.50	Si^+	80	3.75	CH_3SiCl^{37+}
35	9.50	Cl^{35+}	98	4.25	$SiCl_2^{35+}$
37	3.75	Cl^{37+}	102	0.75	$SiCl_2^{37+}$
50	2.25	CH_3Cl^{35+}	113	11.25	$CH_3SiCl_2^{35+}$
52	1.00	CH_3Cl^{37+}	117	2.50	$CH_3SiCl_2^{37+}$
63	13.25	$SiCl^{35+}$	133	2.52	$SiCl_3^{35+}$
65	8.00	$SiCl^{37+}$	139	4.00	$SiCl_3^{37+}$
74	1.50	Cl_2^{37+}	148	6.25	$CH_3SiCl_3^{35+}$
77	1.50	CH_3SiCl^{35+}	154	6.20	$CH_3SiCl_3^{37+}$
78	1.52	CH_3SiCl^{35+}			

The authors thank A. A. Sakovich for assistance in the experimental part of the work.

SUMMARY

1. Methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, ethyltrichlorosilane, diethyldichlorosilane, triethylchlorosilane, phenyltrichlorosilane, methylphenyldichlorosilane and silicon tetrachloride were analyzed with the mass-spectrometer. The nature of their decomposition was established.

2. It was found that decomposition proceeded chiefly by the breaking away of the component which predominated in quantitative relation to silicon – the organic radical or chlorine. In compounds of the $RSiCl_3$ type the probability of rupture of the Si–Cl bond was 2 times greater than of the Si–R bond; in compounds of the R_3SiCl type, the probability of rupture of the Si–R bonds was greater. In compounds of the R_2SiCl_2 type the probability of rupture of the Si–R bond was twice as great as for the Si–Cl bond.

TABLE 6

Dimethyldichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	4.28	Si^+	93	3.22	$(CH_3)_2SiCl^{35+}$
30	2.71	SiH_2^+	95	1.97	$(CH_3)_2SiCl^{37+}$
35	5.80	Cl^{35+}	98	1.93	$SiCl_2^{35+}$
37	2.36	Cl^{37+}	102	3.46	$SiCl_2^{37+}$
42	3.85	$SiCH_2^+$	113	12.6	$CH_3SiCl_2^{35+}$
52	1.84	CH_3Cl^{37+}	117	10.6	$CH_3SiCl_2^{37+}$
63	10.3	$SiCl^{35+}$	128	8.58	$(CH_3)_2SiCl_2^{35+}$
65	6.00	$SiCl^{37+}$	132	9.00	$(CH_3)_2SiCl_2^{37+}$
74	1.8	Cl_2^{37+}			
78	0.86	CH_3SiCl^{35+}			

TABLE 7

Trimethylchlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	3.92	Si^+	63	4.70	$SiCl^{35+}$
30	0.98	SiH_2^+	65	5.08	$SiCl^{37+}$
35	5.30	Cl^{35+}	70	6.80	Cl_2^{37+}
37	2.52	Cl^{37+}	78	3.91	CH_3SiCl^{35+}
39	3.72	–	80	3.53	CH_3SiCl^{37+}
42	4.70	$SiCH_2^+$	93	6.80	$(CH_3)_2SiCl^{35+}$
44	4.50	$SiCH_3H^+$	95	6.75	$(CH_3)_2SiCl^{37+}$
52	3.13	–	108	1.96	$(CH_3)_3SiCl^{35+}$
58	2.04	$(CH_3)_2Si^+$	110	1.92	$(CH_3)_3SiCl^{37+}$

TABLE 8

Ethyltrichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	5.02	Si^+	96	5.66	–
29	3.54	SiH^+	98	6.60	$SiCl_2^{35+}$
35	3.77	Cl^{35+}	102	3.30	$SiCl_2^{37+}$
37	1.89	Cl^{37+}	112	1.89	$CH_2SiCl_2^{35+}$
52	1.94	CH_2Cl^{37+}	116	1.43	$CH_2SiCl_2^{37+}$
63	5.66	$SiCl^{35+}$	127	9.43	$C_2H_5SiCl_2^{35+}$
65	3.77	$SiCl^{37+}$	131	8.50	$C_2H_5SiCl_2^{37+}$
77	0.24	CH_2SiCl^{35}	133	8.95	$SiCl_3^{35+}$
84	1.24	–	139	7.55	$SiCl_3^{37+}$
86	1.94	–	162	3.97	$C_2H_5SiCl_3^{35+}$
92	3.00	$C_2H_5SiCl^{35+}$	168	2.86	$C_2H_5SiCl_3^{37+}$
94	3.07	$C_2H_5SiCl^{37+}$			

TABLE 9

Diethyldichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	5.42	Si^+	77	1.97	CH_2SiCl^{35+}
35	6.42	Cl^{35+}	79	1.87	CH_2SiCl^{37+}
37	3.48	Cl^{37+}	92	3.74	$C_2H_5Si^{35+}$
43	1.22	$SiCH_3^+$	98	5.60	$SiCl_2^{35+}$
44	2.06	$SiCH_3H$	102	5.24	$SiCl_2^{37+}$
52	2.62	CH_2Cl^{37+}	113	1.87	–
56	1.50	$(CH_2)_2Si^+$	121	3.37	$(C_2H_5)_2SiCl^{35+}$
57	1.12	$C_2H_5Si^+$	123	5.24	$(C_2H_5)_2SiCl^{37+}$
63	6.03	$SiCl^{35+}$	127	5.60	$C_2H_5SiCl_2^{35+}$
65	3.30	$SiCl^{37+}$	131	5.66	$C_2H_5SiCl_2^{37+}$
70	0.65	Cl_2^{35+}	156	3.74	$(C_2H_5)_2SiCl_2^{35+}$
74	0.84	Cl_2^{37+}	160	2.80	$(C_2H_5)_2SiCl_2^{37+}$

TABLE 10

Triethylchlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	3.14	Si^+	83	2.54	–
29	3.03	SiH^+	85	1.58	–
30	2.91	SiH_2^+	86	0.97	$(C_2H_5)_2Si^+$
35	2.44	Cl^{35+}	91	1.22	$(CH_2)_2SiCl^{35+}$
37	1.22	Cl^{37+}	92	1.33	$C_2H_5SiCl^{35+}$
39	1.69	–	93	2.66	$(CH_2)_2SiCl^{37+}$
44	1.09	$SiCH_3H$	94	3.14	$C_2H_5SiCl^{37+}$
56	1.45	$(CH_2)_2Si^+$	98	3.38	$SiCl_2^{35+}$
57	0.72	$C_2H_5Si^+$	102	4.24	$SiCl_2^{37+}$
58	0.97	$Si(CH_3)_2^+$	105	4.24	$(CH_2)_2SiCl^{35+}$
59	0.67	–	106	2.90	$C_2H_5CH_2SiCl^{35+}$
60	0.61	–	107	4.28	$(CH_2)_2SiCl^{37+}$
63	4.14	$SiCl^{35+}$	108	3.14	$C_2H_5CH_2SiCl^{37+}$
65	2.14	$SiCl^{37+}$	120	2.91	$C_2H_5(CH_2)_2SiCl^{35+}$
70	1.81	Cl_2^{35+}	121	3.03	$(C_2H_5)_2SiCl^{35+}$
74	1.03	Cl_2^{37+}	122	2.90	$C_2H_5(CH_2)_2SiCl^{37+}$
77	1.39	CH_2SiCl^{35+}	123	3.05	$(C_2H_5)_2SiCl^{37+}$
79	3.06	CH_2SiCl^{37+}	135	3.65	$(C_2H_5)_2CH_2SiCl^{35+}$
81	3.03	–	137	3.63	$(C_2H_5)_2CH_2SiCl^{37+}$

TABLE 11

Phenyltrichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	3.54	Si^+	81	3.54	–
29	3.54	SiH^+	98	0.94	$SiCl^{35+}$
35	6.37	Cl^{35+}	102	1.66	$SiCl_2^{37+}$
37	6.84	Cl^{37+}	108	0.94	–
39	5.66	–	112	0.82	$C_6H_5Cl^{35+}$
42	0.94	–	114	2.01	$C_6H_5Cl^{37+}$
50	5.66	CH_2Cl^{35+}	123	0.82	–
52	5.19	CH_2Cl^{37+}	133	2.01	$SiCl_3^{35+}$
62	2.12	–	139	3.54	$SiCl_3^{37+}$
63	2.10	$SiCl^{35+}$	140	3.54	$C_6H_5SiCl^{35+}$
65	3.54	$SiCl^{37+}$	142	2.60	$C_6H_5SiCl^{37+}$
74	1.06	Cl_2^{37+}	170	6.60	$C_6H_5SiCl_2^{35+}$
76	2.12	–	210	4.72	$C_6H_5SiCl_2^{37+}$
77	3.30	–	216	4.96	$C_6H_5SiCl_3^{37+}$

TABLE 12

Methylphenyldichlorosilane

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	2.16	Si^+	112	2.40	$CH_2SiCl_2^{35+}$
35	3.35	Cl^{35+}	113	2.51	$CH_3SiCl_2^{35+}$
37	3.20	Cl^{37+}	114	2.51	–
43	0.92	CH_3Si^+	116	2.53	$CH_3SiCl_2^{37+}$
50	3.20	CH_3Cl^{35+}	117	1.35	$CH_3SiCl_2^{37+}$
52	3.35	CH_3Cl^{37+}	120	1.40	$C_6H_5SiCH_2^+$
59	0.89	–	140	2.51	$C_6H_5SiCl^{35+}$
63	2.96	$SiCl^{35+}$	142	2.06	$C_6H_5SiCl^{37+}$
65	3.10	$SiCl^{37+}$	154	1.60	–
72	2.50	–	155	2.51	$C_6H_5SiCH_3Cl^{35+}$
74	2.72	Cl_2^{37+}	157	2.83	$C_6H_5SiCH_3Cl^{37+}$
76	3.20	–	160	2.85	–
77	3.20	$C_6H_5^+$	162	2.78	–
88	1.89	–	175	3.10	$C_6H_5SiCl_2^{35+}$
92	2.35	–	179	3.40	$C_6H_5SiCl_2^{37+}$
98	3.05	$SiCl_2^{35+}$	182	2.30	–
102	3.17	$SiCl_2^{37+}$	190	2.82	$C_6H_5CH_3SiCl_2^{35+}$
105	0.89	$C_6H_5Si^+$	194	2.85	$C_6H_5CH_3SiCl_2^{37+}$

TABLE 13

Silicon Tetrachloride

Mass	Content (%)	Formula	Mass	Content (%)	Formula
28	3.92	Si^+	98	3.92	$SiCl_2^{35+}$
35	8.50	Cl^{35+}	102	4.57	$SiCl_2^{37+}$
37	4.57	Cl^{37+}	133	11.80	$SiCl_3^{35+}$
63	9.80	$SiCl^{35+}$	139	15.70	$SiCl_3^{37+}$
65	8.80	$SiCl^{37+}$	168	8.80	$SiCl_4^{35+}$
70	2.62	Cl_2^{35+}	176	14.40	$SiCl_4^{37+}$
74	2.64	Cl_2^{37+}			

3. The probability of rupture of the Si–R bond decreased with enlargement of the radical.

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ON THE THEORY OF TAUTOMERIC EQUILIBRIUM IN SOLUTIONS.

TAUTOMERISM OF THE DIALKYLTHIOPHOSPHATES

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The development of methods for determination of the tautomeric equilibrium constant for rapidly transforming tautomeric systems, such as the lactim-lactams, thion-thiols, etc., is an important problem in the field of tautomerism.

Numerous experimental data indicate as an advantage the fact that the prototropic tautomeric equilibrium of acidic substances (keto-enols, lactim-lactams, thion-thiols) is established, like the protolytic equilibrium of two acids A_IH and $A_{II}H$ which form a common anion A^-, and the solvent S:

$$A_IH + S \rightleftharpoons A^- + HS^+ \rightleftharpoons A_{II}H + S$$

Thus, tautomeric equilibrium represents a triple buffer system, and, as one of us showed [1], it obeys the well-known fundamental laws of acid-base equilibrium in solutions.*

The application of the theory of acid-base protolytic equilibrium to prototropic tautomeric equilibrium enabled us to establish that: 1) the position of the tautomeric equilibrium is determined by the ratio of the ionization constants (protolysis autoprotolysis), of the tautomeric forms in a given medium, and 2) for all tautomeric substances which belong to one type, the ratio of the tautomeric equilibrium constants in two media is a constant value. If K_{TS} is the tautomeric equilibrium constant in solvent S, and K_{A_IS} and $K_{A_{II}S}$ are the ionization constants of the forms, then we can write for the equilibrium in the media S_1 and S_2:

$$K_{TS_1} = \frac{K_{A_IS}}{K_{A_{II}S}}; \quad K_{TS_2} = \frac{K_{A_IS_2}}{K_{A_{II}S_2}} \tag{1}$$

and

$$pK_{TS_1} = pK_{TS_2} + \text{const.} \tag{2}$$

The latter relationship is the equally well-known empirical formula of K. Meyer [3], $K_{TS} = EL$. It was derived from (1) by the use of the Brönsted formula [4].

$$pK_{AS_1} = pK_{AS_2} + C \tag{3}$$

(in which C is a constant characteristic of each type of acid [5]), referring to the tautomeric forms A_IH and $A_{II}H$ as to acids of two different chemical types (i.e., with different C_1 and C_2).

On the basis of the relationships cited, Kabachnik and Ioffe [6] developed a potentiometric method for determination of the position of the tautomeric equilibrium. If the constants C_1 and C_2 of equation (3) for substances of the type A_IH and $A_{II}H$ are known, then on the basis of measurement of the apparent ionization constant of a given equilibrium mixture, $A_IH + A_{II}H$ in two solvents S_1 and S_2 ($K_{A_IA_{II}S_1}$ and $K_{A_IA_{II}S_2}$), we can calculate the tautomeric equilibrium constants K_{TS_1} and K_{TS_2} from the formula:

$$K_{TS_1} = \frac{K_{A_IA_{II}S_1} - C_1K_{A_IA_{II}S_2}}{C_2K_{A_IA_{II}S_2} - K_{A_IA_{II}S_1}}, \tag{4}$$

$$K_{TS_2} = K_{TS_1} \cdot \frac{C_2}{C_1}. \tag{5}$$

knowing the same tautomeric equilibrium constants K_{TS_1} and K_{TS_2} we can also calculate the ionization constants of each of the forms in each of the solvents

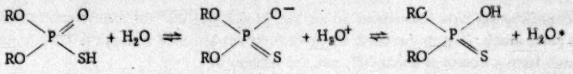
* The general theory of tautomeric equilibrium and the reactivity of tautomeric substances was considered in the works of A. N. Nesmeyanov and one of us [2].

$$K_{A_I S} = K_{A_I A_{II} S}(K_{TS} + 1), \quad (6)$$

$$K_{A_{II} S} = \frac{K_{A_I A_{II} S}(K_{TS} + 1)}{K_{TS}}. \quad (7)$$

The method was successfully applied by the authors in the instance of a keto-enolic equilibrium, i.e., an equilibrium which was established slowly. However, since the method of measurement of the apparent ionization constant of equilibrium mixtures does not involve a disruption of the equilibrium, we cannot question its applicability also to rapidly transforming tautomeric systems. In addition to this, the establishment of constants C_1 and C_2, characteristic of acids of the type $A_I H$ and $A_{II} H$ is a basic problem. One method of their determination includes the application of certain standard acids, which also belong to the types $A_I H$ and $A_{II} H$, but which are not tautomeric.

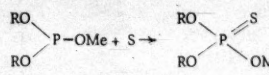
As an object of investigation in the present work we chose the dialkylthiophosphates, the tautomeric equilibrium of which, for example in water, can be represented as follows:



(I) (II)

Our choice was made on the basis of the following assumptions. Like the thion-thiolic tautomeric system, the dialkylthiophosphates should belong to the rapidly transforming type; they should also be rather strong acids; we should not expect from them, in contrast to thiocarboxylic acids, easy hydrolyzability in an aqueous medium. Furthermore, thanks to the similarity of the acid properties of the oxygen and sulfur acids of phosphorus, we can expect that the position of the tautomeric equilibrium will not be shifted strongly toward any one side.

The salts of the dialkylthiophosphoric acids have been described many times in the literature [8]. However, the free acids have not been described. We obtained them in the pure form, and their properties confirmed our assumptions. We carried out the production of the salts of the dialkylthiophosphoric acids by Foss' modified method [9], by the addition of sulfur to salts of the dialkylphosphorous acids:



We isolated the free dialkylthiophosphoric acids from the sodium or triethylammonium salts. The constants of the resulting dialkylthiophosphoric acids (mixture of two isomers) are cited in Table 1.

TABLE 1

No.	Formula	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	MR_D	
					found	calculated**
1	$(C_2H_5O)_2PSOH$	106-107° (2.5)	1.4719	1.1806	40.36	40.04
2	$(C_3H_7O)_2PSOH$	108.5-109.5 (0.009)	1.4678	1.1022	49.97	49.28
3	$(iso\text{-}C_3H_7O)_2PSOH$	89-90 (1.5)	1.4592	1.0906	49.65	49.28
4	$(iso\text{-}C_4H_9O)_2PSOH$	75-76 (0.008)	1.4670	1.0670	58.88	58.52

Since Form (I) of the dialkylthiophosphates belongs to the class of the thiolic acids of phosphorus, and Form (II) belongs to the oxygen acids of phosphorus, we chose the dialkyldithiophosphates (III) and the dialkylphosphates (IV), for which tautomerism was impossible, as standards for the determination of C_1 and C_2.

(III) (IV)

* The fact that the anion $(RO)_2PSO^-$ has the structure presented above results from the data of Gore's spectral investigation [7].

** The MR_D values were calculated for the thionic isomer $(RO)_2PS(OH)$. They were somewhat higher for the thiolic isomer $(RO)_2PO(SH)$.

The dialkyldithiophosphates were studied in the pure form by Kabachnik and Mastryukova [10]. In the present work they were prepared by a method described in the article indicated.

The dialkylphosphates were described in the literature as impure syrups. Only Toy [11] purified diethylphosphate, by distillation of the syrup at high vacuum; however, he did not give the constants of this substance. The dialkylphosphates which we prepared according to Toy and distilled at high vacuum are listed below in Table 2.

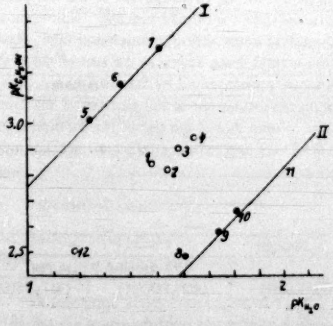
TABLE 2

No.	Formula	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated
5	$(CH_3O)_2POOH$	79-80° (0.0001)	1.4049	1.3337	23.15	23.32
6	$(C_2H_5O)_2POOH$	87 (0.0001)	1.4169	1.1800	32.81	32.55
7	$(C_3H_7O)_2POOH$	94 (0.0001)	1.4251	1.1043	42.10	41.79

We measured the ionization constants with a glass electrode by the potentiometric method. All the measurements were made in aqueous solutions which contained 7% alcohol, and in solutions of 80% alcohol. The dialkyldithiophosphates proved to be rather strong acids with ionization constants of the order of 10^{-2} in aqueous solution and 10^{-3} in alcoholic solutions (Table 3).

TABLE 3

No.	Formula	Solvent: water		Solvent: 80% alcohol	
		pK_{H_2O}	$K_{H_2O} \cdot 10^2$	$pK_{C_2H_5OH}$	$K_{C_2H_5OH} \cdot 10^3$
8	$(C_2H_5O)_2PSSH$	1.62	2.40	2.48	3.31
9	$(C_3H_7O)_2PSSH$	1.75	1.78	2.57	2.69
10	$(iso\text{-}C_3H_7O)_2PSSH$	1.82	1.51	2.65	2.24
11	$(iso\text{-}C_4H_9O)_2PSSH$	2.00	1.00	2.81	1.55



The relation of $pK_{C_2H_5OH}$ to pK_{H_2O} is given in the Figure. As seen from the graph (Line II), the characteristic ionization constants of the dithio acids which we studied satisfied the Brönsted equation very well (linear relation; $\tan\alpha = 1$). The value of $C_1 = 6.76$ was calculated from experimental data.

The dialkylphosphates in aqueous solution were stronger acids than were the corresponding dithio acids (Table 4); however, the difference in the ionization constants was small. In an alcoholic medium they were less strong acids, with ionization constants of the order of 10^{-4}.

The characteristic ionization constants also satisfied the linear relation for $\tan\alpha = 1$ very well (see Figure, Line I). The value of $C_2 = 58.9$ was calculated from experimental data.

The dialkylthiophosphates (equilibrium mixture of isomers), as also should be expected, occupy an intermediate position between the dialkyldithiophosphates and the dialkylphosphates (Table 5).

It is evident from the Figure that Points 1, 2, 3, 4 and 12, which correspond to the monothiophosphates, are located between Lines I and II. The tautomeric equilibrium constants of the dialkylthiophosphates which were calculated from formulas (4) and (5) are presented in Table 6.

Let us turn our attention to the stability of the tautomeric equilibrium constants, in water and in alcohol, for all the homologs measured (within the limits of experimental error). This result is found to be in agreement with the data of Arndt, Loewe and Ginkök [12] on the keto-enolic equilibrium constants of homologous esters of

TABLE 4

No.	Formula	Solvent			
		water		80% alcohol	
		pK_{H_2O}	$K_{H_2O} \cdot 10^2$	$pK_{C_2H_5OH}$	$K_{C_2H_5OH} \cdot 10^4$
5	$(CH_3O)_2POOH$	1.25	5.62	3.01	9.77
6	$(C_2H_5O)_2POOH$	1.37	4.27	3.15	7.08
7	$(C_3H_7O)_2POOH$	1.52	3.02	3.29	5.13

TABLE 5

No.	Formula	Solvent			
		water		80% alcohol	
		pK_{H_2O}	$K_{H_2O} \cdot 10^2$	$pK_{C_2H_5OH}$	$K_{C_2H_5OH} \cdot 10^5$
12	$(CH_3O)_2PSOH$*	1.18	6.61	2.50	3.16
1	$(C_2H_5O)_2PSOH$	1.49	3.24	2.84	1.45
2	$(C_3H_7O)_2PSOH$	1.55	2.82	2.82	1.51
3	$(iso\text{-}C_3H_7O)_2PSOH$	1.59	2.57	2.90	1.26
4	$(iso\text{-}C_4H_9O)_2PSOH$	1.65	2.24	2.94	1.16

TABLE 6

No.	Formula	Equilibrium constants K_{TS} $(RO)_2PO(SH) \rightleftarrows (RO)_2PS(OH)$	
		in water	in alcohol
12	$(CH_3O)_2PSOH$	0.38	3.32
1	$(C_2H_5O)_2PSOH$	0.42	3.76
2	$(C_3H_7O)_2PSOH$	0.31	2.67
3	$(iso\text{-}C_3H_7O)_2PSOH$	0.35	3.01
4	$(iso\text{-}C_4H_9O)_2PSOH$	0.32	2.80

acetoacetic acid. Whereas the concentrated esters were characterized by sharp fluctuations of the equilibrium constant (from 0.056 to 0.181), in dilute solutions the equilibrium constant was the same for all the esters. The constancy obtained should be attributed to the equality of the influence of the ester radical on the strength of both tautomeric acids (in our case the SH-acids and the OH-acids; in the case studied by Arndt and coworkers, on the strength of the ketonic and enolic forms as acids).

Furthermore, it follows from the data of Table 6 that in aqueous solution the equilibrium was shifted toward the thiolic form (I), but in alcoholic solution it was shifted toward the thionic form (II).

From the data obtained, using formulas (6) and (7), we calculated the ionization constants of the thiolic and thionic forms in aqueous and in alcoholic solutions. The results are cited in Table 7.

As also should be expected, the thiolic acids were weaker than the thionic acids in aqueous solution, but they were stronger in alcoholic solution. This agreed with the fact that the dithio acids $(RO)_2PSSH$ are weaker in aqueous solutions, but in alcoholic solution they are stronger than their oxygen analogs $(RO)_2POOH$. Thus, to a great extent we were able to elucidate the tautomeric relationships of the dialkylthiophosphates.

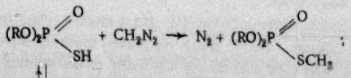
It seemed to us expedient to compare the results obtained with data from the investigation of the chemical properties of dialkylthiophosphate solutions, particularly data on their reactions with diazomethane. Numerous investigations of Arndt and coworkers [13] showed that reactions of tautomeric acids with diazomethane take place, in the first place, with the non-ionized forms of the acids, second, the methyl group forms at the site of the hydrogen of the acid, and third, the stronger the acids the more rapidly they were methylated by diazomethane. The diazomethane method was widely employed by Arndt and coworkers for determination of the position of the tautomeric equilibrium in solutions. In connection with this, it is necessary to note that if the use of the method is justified for a slowly transforming tautomeric system, then it can give only very approximate information for rapidly transforming tautomers.

TABLE 7

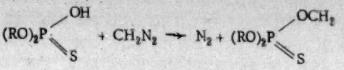
No.	Formula	Solvent			
		water $K_{H_2O} \cdot 10^2$		80% alcohol $K_{C_2H_5OH} \cdot 10^5$	
		$(RO)_2PO(SH)$	$(RO)_2PS(OH)$	$(RO)_2PO(SH)$	$(RO)_2PS(OH)$
12	$(CH_3O)_2PSOH$	9.20	24.1	13.6	4.10
1	$(C_2H_5O)_2PSOH$	4.60	10.8	6.90	1.84
2	$(C_3H_7O)_2PSOH$	3.72	12.1	5.51	2.06
3	$(iso\text{-}C_3H_7O)_2PSOH$	3.45	9.97	5.10	1.69
4	$(iso\text{-}C_4H_9O)_2PSOH$	2.97	9.25	4.40	1.57

* The measurements were made, not with the free acid, but with the sodium salt $(CH_3O)_2PSONa$.

The reaction of the tautomeric dialkylthiophosphates with diazomethane may be represented by the following scheme:



(V) R = C_2H_5



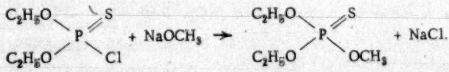
(VI) R = C_2H_5

Following Arndt, we assumed that methylation by diazomethane takes place without a transference of reaction center. If this is so, then on methylation of an equilibrium mixture of the dialkylthiophosphates, both isomeric methylation products should form. As to their relative quantities, they can correspond to the equilibrium quantities only under conditions of equality of the rate constants of both forms reacting with diazomethane, which is not very likely.

An ether solution of diethylthiophosphate rapidly decolorized a solution of diazomethane; in addition, the two possible methylation products (V) and (VI) formed in a 4:1 ration; the total yield, moreover, was 91.4%. No other distillable reaction products formed on methylation.*

We also synthesized the methylation products by a known method. Substance (V) was prepared by methylation of the sodium salt of diethylthiophosphoric acid with methyl iodide; moreover, the formation of the S-derivatives was demonstrated earlier [14]:

We obtained the isomeric O-methyl ester (VI) by direct synthesis from diethylchlorothionphosphate and sodium methylate:



The constants of both substances, obtained by different methods, agreed well (Table 8).

TABLE 8

Substance	B.p. under pressure (mm)	n_D^{20}	d_4^{20}
S-methyl ester:			
From reaction with CH_2N_2	128° (26)	1.4607	1.1418
Known	78.5-79 (3)	1.4607	1.1430
O-methyl ester:			
From reaction with CH_2N_2	103.5-104.5 (26)	1.4523	1.1071
Known	81.5-82 (10)	1.4529	1.1076

As indicated above, the result of methylation by diazomethane cannot be considered as a quantitative characteristic of the position of the tautomeric equilibrium. However, it demonstrated the presence of tautomeric equilibrium of the dialkylthiophosphates.

* We also attempted to produce the methyl esters of sodium salts of diethylthiophosphoric acid by methylation with diazomethane in aqueous solution (see experiments of Kuhn and others [15]). In this case the yield of methylation products was very low (38%), and it consisted of only one S-methyl ester.

EXPERIMENTAL

Sodium dimethylmonothiophosphate was obtained by Foss' procedure [9].

Preparation of the dialkylthiophosphates (I ⇌ II). In a three-necked flask with a stirrer, reflux condenser and dropping funnel, closed by calcium chloride tubes, we placed dialkylphosphite and sulfur, taken in equimolar quantities, and added anhydrous ether (100-120 ml per 0.5 mole of the starting materials). With vigorous stirring, dry triethylamine in ether solution was added dropwise. After addition of the first 3-5 g of the ether solution, the ether in the reaction flask began to boil; by addition of triethylamine, the boiling of the ether was continued until the end of the reaction. At the end of the reaction all the sulfur had dissolved. The ether solution was diluted with cold water.* Then the ether layer was separated, and the water layer was cooled in a mixture of snow and salt, and decomposed by an excess of cold, concentrated hydrochloric acid. The dialkylmonothiophosphoric acid which formed was salted out by the addition of ammonium chloride, and was extracted with benzene. The benzene solution was dried over calcined sodium sulfate and fractionated in vacuo.

O,O-Diethylthiophosphate was obtained from 69.5 g (0.5 mole) of diethylphosphite, 50.5 g (0.5 mole) of triethylamine, and 16 g (0.5 mole) of sulfur. Hydrochloric acid 100 ml. B.p. 106-107° at 2.5 mm, n_D^{20} 1.4719, d_4^{20} 1.1806. The yield was 46 g (54%).

Found: MR_D 40.36; equiv. 168.5, 167.0. Calculated: MR_D 40.04; equiv. 170.2.

Found %: C 28.25, 28.39; H 6.65, 6.76. $C_4H_{11}O_3PS$. Calculated %: C 28.23; H 6.52.

O,O-Dipropylthiophosphate was obtained from 16.6 g (0.1 mole) of dipropylphosphite, 10.1 g (0.1 mole) of triethylamine, and 3.2 g (0.1 mole) of sulfur. Hydrochloric acid 20 ml. B.p. 108.5-109.5° at 0.09 mm, n_D^{20} 1.4678, d_4^{20} 1.1022. The yield was 12.3 g (62%).

Found: MR_D 49.97; equiv. 199.6, 198.7. Calculated: MR_D 49.28; equiv. 198.2.

Found %: C 36.21, 36.56; H 7.82, 7.86; S 15.54, 16.08; P 15.75, 15.56. $C_6H_{15}O_3PS$. Calculated %: C 36.35; H 7.63; S 16.18; P 15.63.

O,O-Diisopropylthiophosphate was obtained from 12.4 g (0.075 mole) of diisopropylphosphite, 8.6 g (0.086 mole) of triethylamine, and 2.4 g (0.075 mole) of sulfur. Hydrochloric acid 20 ml. B.p. 89-90° at 1.5 mm, n_D^{20} 1.0906, d_4^{20} 1.4592. The yield was 10.8 g (72%).

Found: MR_D 49.65; equiv. 198.5, 197.6. Calculated: MR_D 49.28; equiv. 198.2

Found %: C 36.33, 36.78; H 7.64, 7.53; S 15.78, 16.00; P 15.40, 15.75. $C_6H_{15}O_3PS$. Calculated %: C 36.35; H 7.63; S 16.18; P 15.63.

O,O-Dibutylthiophosphate was prepared from 5.7 g (0.029 mole) of dibutylphosphate, 3.43 g (0.034 mole) of triethylamine, 0.93 g (0.029 mole) of sulfur. Hydrochloric acid 8 ml. B.p. 75-76° at 0.008 mm, n_D^{20} 1.4670, d_4^{20} 1.0670. Yield, 6.1 g (77%).

Found: MR_D 58.88; equiv. 228.6, 229.5. Calculated: MR_D 58.52; equiv. 226.3.

Found %: C 42.65, 42.65; H 8.78, 8.77; P 13.57, 13.55; S 13.80, 14.06. $C_8H_{19}O_3PS$. Calculated %: C 42.46; H 8.46; P 13.69; S 14.17.

Production of the dialkylphosphates (IV). The synthesis of the dialkylphosphates was carried out exactly according to Toy's procedure [11]. In order to purify the resulting syrupy substance, it was distilled at high vacuum.

Dimethylphosphate. B.p. 79-80° at $1 \cdot 10^{-4}$ mm, n_D^{20} 1.4049, d_4^{20} 1.3337.

Found: MR_D 23.15; equiv. 125.0, 124.6. Calculated: MR_D 23.32; equiv. 126.1.

Found %: P 24.32, 24.76. $C_2H_7O_4P$. Calculated %: P 24.60.

Diethylphosphate. B.p. 87° at $1 \cdot 10^{-4}$ mm, n_D^{20} 1.4169, d_4^{20} 1.1800.

Found: MR_D 32.81; equiv. 154.5, 154.1. Calculated: MR_D 32.55; equiv. 154.1.

Found %: P 20.42, 20.50. $C_4H_{11}O_4P$. Calculated %: P 20.13.

* The diethylthiophosphate solution was not diluted with water, but on cooling to −20° the salt separated as a film.

Dipropylphosphate. B.p. 94° at $1 \cdot 10^{-4}$ mm, n_D^{20} 1.4251, d_4^{20} 1.1043.

Found: MR_D 42.10; equiv. 183.2, 183.0. Calculated: MR_D 41.79; equiv. 182.1.

Found %: P 17.14, 17.20. $C_8H_{19}O_4P$. Calculated %: P 17.03.

Determination of the ionization constants. The ionization constants were calculated from the data of pH measurements of partially neutralized solutions of the substances in water, which contained 7% alcohol,* and in 80% (by volume) alcohol. The measurements were made with a glass electrode by a tube potentiometer. All the measurements were made at 20°; the accuracy of the measurements was about 0.04 pH unit. The concentrations of the solutions to be measured were 0.005 M. We made several measurements for each substance at three different degrees of neutralization. Because of the small value of the quantity $k_W/[H^+]$, the calculation was made from a simplified formula [16]:

$$K_{AS} = [H^+] \frac{[Na^+] + [H^+]}{M - ([Na^+] + [H^+])}.$$

Methylation of diethylthiophosphate by diazomethane. A solution of 34.4 g (0.1 mole) of diethylthiophosphate in 100 ml of ether was added dropwise to an ether solution of diazomethane (from 33 g of nitrosomethylurea) in 500 ml of ether. On completion of the reaction, the ether solution was dried over sodium sulfate, the ether was removed and the residue was vacuum distilled. The b.p. was 113-120.5° at 19-22 mm, n_D^{20} 1.4589, d_4^{20} 1.1334. 33.7 g (91.4%) of a crude mixture was obtained.

The product was fractionated twice in vacuo from a column with an efficiency of 18 theoretical plates.

O,O-Diethyl-O-methylthionphosphate. B.p. 103.1-104.5° at 26 mm, n_D^{20} 1.4523, d_4^{20} 1.1071. MR_D 44.91; calculated 44.78.

Found %: C 32.43, 32.58; H 7.29, 7.09; P 16.84, 16.56. $C_5H_{13}O_3PS$. Calculated %: C 32.60; H 7.11; P 16.82.

O,O-Diethyl-S-methylthiolphosphate. B.p. 127.5-128° at 26 mm, n_D^{20} 1.4607, d_4^{20} 1.1418. MR_D 44.23; calculated 44.25.

Found %: C 32.74, 32.54; H 7.33, 7.32; P 16.85, 16.88; S 17.25, 17.16. $C_5H_{13}O_3PS$. Calculated %: C 32.60; H 7.11; P 16.82; S 17.41.

Methylation of sodium diethylthiophosphate by diazomethane in aqueous solution. 100 ml of a benzene solution of diazomethane, obtained from 45 g of nitrosomethylurea in 500 ml of benzene was added by portions to a solution of the sodium salt of diethylthiophosphoric acid in 400 ml of water. After addition of each portion, the benzene layer was separated, and the aqueous layer was neutralized toward phenolphthalein with hydrochloric acid. The combined benzene solutions were dried with sodium sulfate and fractionated. On distillation, only the one fraction with a b.p. of 126-127° at 26 mm, n_D^{20} 1.4607, d_4^{20} 1.1425 was obtained. The yield was 14.0 g (38%).

Production of O,O-diethyl-S-methylthiolphosphate (V). 21.3 g (0.15 mole) of methyl iodide was added dropwise to 9.6 g (0.05 mole) of sodium diethylthiophosphate in 120 ml of dry chloroform. The solution was boiled on the water bath for 3 hours. The sodium iodide was filtered off and washed with chloroform. The weight of NaI was 5.7 g. After drying of the mother liquor and removal of the solvent, the residue was distilled at 103-103.5° at 10 mm. The yield was 8.2 g (89%). A second distillation was made at 78.5-79° at 3 mm.

n_D^{20} 1.4607, d_4^{20} 1.1430. MR_D 44.15; calculated 44.25 (AR_S 8.6). Schrader [17] cites for this substance, b.p. 112-113° at 14 mm.

Found %: P 17.11. $C_5H_{13}O_3PS$. Calculated %: P 16.85.

Production of O,O-diethyl-O-methylthionphosphate (VI). 29.7 g of diethylchlorothionphosphate (prepared according to Fletcher [18]) was added dropwise to a solution of sodium methylate (3.6 g of sodium in 45 ml of methyl alcohol). The mixture was heated at 50° for half an hour. The NaCl was filtered off (weight was 9.04 g – 98%), and the filtrate was dried. After removal of the solvent the residue was distilled at 85° at 10 mm. The yield was 25.1 g (86.5%). After a second distillation the b.p. was 81.5-82° at 10 mm.

n_D^{20} 1.4529, d_4^{20} 1.1076, MR_D 44.89; calculated 44.78.

Found %: C 32.45, 32.36; H 7.48, 7.25; P 16.42, 16.70; S 17.01, 17.43. $C_5H_{13}O_3PS$. Calculated %: C 32.60; H 7.11; P 16.82; S 17.41.

* Because of the limited solubility of some of the substances in water, all the measurements were made in 7% alcohol.

SUMMARY

1. The free dialkylthiophosphoric acids were synthesized, and their ionization constants in an aqueous solution and in a solution of 80% alcohol were determined. The dialkylphosphoric acids were obtained in the pure form and their ionization constants, and also the ionization constants of the dialkyldithiophosphoric acids in the same solvents, were determined.

2. On the basis of the measurements made, the tautomeric equilibrium constants of the dialkylthiophosphoric acids in an aqueous solution and in a solution of 80% alcohol were calculated. The ionization constants of the thionic and thiolic forms of these acids were also calculated.

3. The reaction of diethylthiophosphoric acid with diazomethane was studied. It was shown, moreover, that the two possible methylation products, the O,O-diethyl-S-methylthiolphosphate and the O,O-diethyl-O-methylthionphosphate, formed in a 4:1 ratio, which confirmed the tautomerism of the dialkylthiophosphates.

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* See Consultants Bureau Translation, page 37.

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THE PROBLEM OF THE STUDY OF THE MECHANISM OF ESTERIFICATION OF ETHYL ALCOHOL ON ACTIVATED COPPER CATALYSTS

V. THE EFFECT OF HYDROGEN ON THE REACTION RATE

B. N. Dolgov, T. V. Nizovkina and I. M. Stroiman

In the study of the dehydrogenation reaction of ethyl alcohol on activated copper catalysts, with the formation of acetaldehyde, the elucidation of the role of hydrogen is of interest. It has been observed by many authors that the presence of hydrogen, especially if it is introduced supplementarily to the hydrogen which forms because of the dehydrogenation reaction, has a favorable effect on the course of the process, diminishing the role of side reactions and favoring smoother progress of the main reaction.

It was shown by experiments on the esterification of isoamyl alcohol [1] that hydrogen added to the reaction mixture promotes an increase of the yield of ester and a decrease of the yield of isovaleraldehyde. From our point of view, the role of hydrogen in the dehydrogenation reaction appears to be chiefly its influence on the rate of the diffusion process which, according to our investigations, determined the rate of the esterification reaction [2] on our activated catalysts.

In the present work we studied the effect of hydrogen on the rate of the acid-free esterification of ethyl alcohol. Experiments with additions of hydrogen were carried out under conditions analogous to those made without additional hydrogen [2]. Activated copper catalyst was charged into a reactor, a hard glass tube. The volume occupied by the catalyst in the reactor amounted to 11 ml. A copper catalyst on which previous experiments were carried out served as the catalyst. Hydrogen was supplied to the reactor steadily, simultaneously with the introduction of alcohol. The experiments with different volumerrates were carried out at 22°. The data obtained are in Table 1.

TABLE 1

Experiments on the Study of the Effect of Hydrogen on the Esterification of Alcohol at 220°

Expt. No.	Duration of expt. (mins.)	Quantity of alcohol supplied (92.65%)		Quantity of hydrogen supplied per expt. (liters)	Ratio of alcohol to hydrogen	Total obtained		Quantity of liquid products obtained (g)				
		g/min	millimoles/min. on conversion to 100% alcohol			liquid condensate	gas under standard conditions (liters)	acetic acid	ethyl acetate	acetaldehyde	ethyl alcohol	acetone
1	30	0.1305	2.610	0.476	4.4:1	3.67	1.620	0.070	1.674	0.332	1.26	0.051
2	30	0.198	3.900	0.470	6.7:1	5.59	1.930	0.063	2.016	0.425	2.662	0.056
3	30	0.125	2.610	1.850	1.1:1	3.90	1.660	0.0447	0.760	0.604	1.931	0.042
4	60	0.06	1.300	0.932	2.3:1	4.05	1.864	0.067	1.698	0.234	1.729	0.071
5	120	0.033	0.650	1.846	1.1:1	3.53	2.520	0.0054	1.632	0.156	1.600	0.026
6	240	0.0165	0.325	3.652	1:1.7	4.06	2.240	0.406	1.610	0.452	2.060	0.083

It is evident from a comparison of the course of the esterification with and without hydrogen (Fig. 1), that the extent of conversion of alcohol for experiments with hydrogen is similar to that without hydrogen. The percentage of acetaldehyde in the reaction products was somewhat less in the experiments with hydrogen (Fig. 2), and the percentage yield of ethyl acetate (Fig. 3) in the experiments with hydrogen was somewhat higher than in those without it.

In the study of the effect of hydrogen on the diffusion rate it is necessary to calculate the diffusion coefficient and the concentration gradient of the diffusing substance, according to the equation:

$$dm = -DS \frac{dc}{dl} dt,$$

where dm is the mass of the substance, D is the diffusion coefficient, S is the area through which the substance diffuses, dc/dl is the concentration gradient, and dt is the time interval. In its turn, the concentration gradient of the alcohol, on additional introduction of hydrogen, is determined by the decrease of the concentration of the alcohol in the gas volume and by the depth of the diffusion layer, which decreases with an increase of the volume rate of the gas mixture during the introduction of additional hydrogen. The diffusion coefficient has decisive value, since the concentration gradient changes very little because of the fact that the concentration of the alcohol and the depth of the diffusion layer change proportionally to each other.

An increase of the hydrogen concentration, as a result of its addition, produced an increase of the diffusion coefficient of the alcohol. In order to account for this, the diffusion coefficient in relation to the partial pressure of hydrogen was calculated for four experiments (1, 3, 4 and 6).

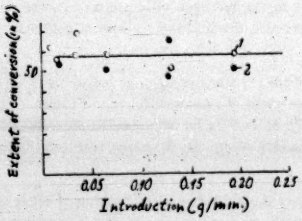

Fig. 1. Extent of conversion of alcohol in relation to introduction. 1) Without hydrogen; 2) with hydrogen.

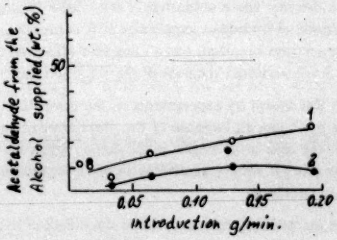

Fig. 2. Percentage content of acetaldehyde from the quantity of alcohol in relation to introduction. 1) Without hydrogen; 2) with hydrogen.

A method proposed by Gilliland [3] was used for the calculation. His empirical formula was a modification of the Maxwell formula. In the Gilliland equation, the radius of the colliding molecules was replaced proportionally by the cube root value of the molar volumes of the liquid substances.

$$D_{AB} = 0.0043 \frac{T^{3/2}}{(V_A^{1/3} + V_B^{1/3})^2 P} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}},$$

where D is the diffusion coefficient; T is the absolute temperature; P is the total pressure; M_A and M_B are the molecular weights of the alcohol and of the mixture which consisted of the reaction products; V_A and V_B are the molar volumes of the alcohol and the average molar volume of the mixture of reaction products, without alcohol, at their standard boiling points, entering into the mixture of substances. The molar volumes entering into the equation were calculated by Kopp's Law, from the sum of the atomic volumes of the individual gram-atoms, for which we used the rule and the values of each substance given by Arnold [4]. The value of the molar volume for ethyl alcohol was calculated from data from the table cited in Hougen and Watson's monograph [5]. These values were added up as follows:

$$V_{CH_3C_2OH} = 2(14.8) + 6(3.7) + 7.4 = 59.2.$$

The second molar volume in the equation, which corresponded to the mixture of reaction products, was worked out by means of calculation of the average values from the analytical data of the condensate obtained for all the substances, with the exception of alcohol, as assumed in calculations of the diffusion coefficient of one substance from a mixture of several other substances. For example, for the calculation of the average molar volume of a mixture of the reaction products from experiment 1, according to Table 1, the composition of the condensate minus the ethyl alcohol was used. The weight of each component was converted to millimoles/minute. The corresponding molar volumes for the complex molecules were calculated from the tables [5]. The partial molar volumes were calculated by multiplication of the molar volume of the pure substance by a fraction which corresponded to the component in the reaction mixture. The partial molar volumes were added up and divided by the total number of millimoles which corresponded to this sum. Thus, the molar volume of one mole of the mixture of reaction products was calculated.

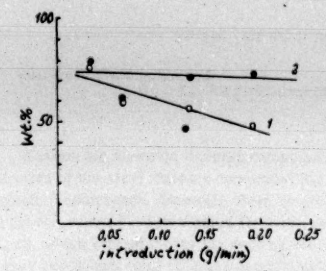

Fig. 3. Relation of the yield of ethyl acetate (wt. %) to the extent of conversion of the alcohol. 1) Without hydrogen; 2) with hydrogen.

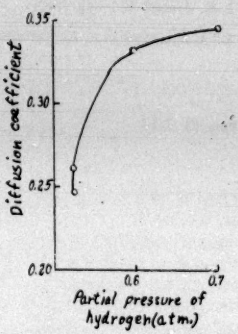

Fig. 4. Relation of the diffusion coefficient to the partial pressure of hydrogen.

The molecular weight of the components entering into the equation was obtained as the molecular weight of ethyl alcohol and the average molecular weight of a mixture of the reaction products without ethyl alcohol. The total pressure P was calculated as the average of the sum of the partial pressures of the components obtained in the experiment, the ethyl alcohol and hydrogen supplied to the reactor per 1 minute. The pressure was compared to 1 atm.

The values of the diffusion coefficients obtained for all four experiments are cited in Table 2.

TABLE 2

Calculation of the Diffusion Coefficient in Experiments with Alcohol for Different Ratios of Alcohol and Hydrogen

Expt. No.	Molar ratio of alcohol : hydrogen	Average molecular wt. of mixture	Average molar volume of mixture	Diffusion coefficient
1	4.4:1	20.80	33.0	0.247
2	2.3:1	18.80	31.0	0.261
3	1.1:1	12.20	23.7	0.332
4	0.6:1	10.80	23.0	0.350

From the data obtained for the diffusion coefficients, a curve of the relation of these coefficients to the partial pressure of hydrogen was plotted (Fig. 4). The diffusion coefficient also increased with an increase of the partial pressure of hydrogen (Fig. 4), which indicates an increase of the reaction rate. The increase of the diffusion coefficient compensated for the decrease of contact time, and as a result a constancy of the extent of conversion of alcohol was obtained both in the experiments with and without addition of hydrogen. An effect of hydrogen was still indicated, provided that the surface of the catalyst was cleaned at the time of the same experiment, and the activity of the catalyst was made more stable.

SUMMARY

The addition of hydrogen to a reaction mixture in the acid-free esterification of ethyl alcohol did not produce a change of the extent of the conversion of the alcohol, which was explained, according to our concept of the mechanism of this catalytic reaction, by the increase of the coefficient of diffusion of the substances through the reaction mixture at increased hydrogen contents. This was confirmed by the diffusion coefficient calculated from Gilliland's empirical formula.

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NEW METHOD OF SYNTHESIS OF ALKYL COMPOUNDS OF MERCURY

FROM MERCURIC SALTS OF ORGANIC ACIDS

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Whereas for aromatic mercury compounds there are a large number of convenient methods of synthesis [1], the production of the alkyl mercury compounds has been limited to the amalgam method and to synthesis via the organomagnesium compounds. However, these methods also have a number of intrinsic disadvantages. In a preceding report [2] we proposed a new method for synthesis of the methyl compounds of mercury, based on the reaction of methyl radicals, which formed during the decomposition of acetyl peroxide, with metallic mercury. By this method organomercury compounds were obtained in sufficiently high yield; however, the method had the following disadvantages: first, a large quantity of mercury, as compared with the quantity of mercury reacting, had to be used; and second, a relatively large quantity of acetyl peroxide had to be synthesized. It seemed to us to be of interest to extend our investigation in the direction of development of the most convenient methods of synthesis of organomercury compounds. For this purpose, it was necessary to investigate the reaction of fixation of the alkyl radicals in the liquid phase.

In the present work we demonstrated that mercurous acetate, obtained by the action of acetyl peroxide on mercury in the cold, reacts with acetyl peroxide on heating in a benzene solution, with the formation of methylmercury acetate.

The yield amounted to about 49%, on the basis of the peroxide used. This compound was also obtained in high yield by the action of acetyl peroxide on mercuric acetate.

Since the isolation of acetyl peroxide in the pure form presents a number of disadvantages in connection with its high explosiveness, we used a benzene-acetic solution of acetyl peroxide in the present work.

For mercurous acetate the reaction proceeds according to the equation:

$$(CH_3CO_2)_2 + CH_3-\underset{\underset{O}{\|}}{C}-O-Hg-Hg-O-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow 2CO_2 + 2CH_3HgOCOCH_3.$$

The mechanism of this process may be represented in this way:

$$(CH_3CO_2)_2 \rightarrow 2CH_3CO_2\cdot$$

$$CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$$

$$CH_3-\underset{\underset{O}{\|}}{C}-O-Hg-Hg-O-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3\cdot \rightarrow CH_3HgO\underset{\underset{O}{\|}}{C}CH_3 + CH_2\underset{\underset{O}{\|}}{C}-OHg\cdot$$

$$2CH_3COOHg\cdot \rightarrow CH_3\underset{\underset{O}{\|}}{C}-O-Hg-Hg-O-\underset{\underset{O}{\|}}{C}CH_3.$$

By the use of this mechanism, the following is indicated. No methylmercury acetate formed on prolonged heating of mercurous acetate in benzene. A similar process takes place between the phenyl-radical and mercurous acetate on conducting the same reaction with benzoyl peroxide in benzene

$$CH_3\underset{\underset{O}{\|}}{C}-O-Hg-Hg-O-\underset{\underset{O}{\|}}{C}CH_3 + C_6H_5\cdot \rightarrow C_6H_5HgO\underset{\underset{O}{\|}}{C}CH_3 + CH_3\underset{\underset{O}{\|}}{C}OHg\cdot$$

and further according to the preceding equation.

The yield of phenylmercury acetate was 29%, on the basis of the benzoyl peroxide; the remaining portion of the benzoyl peroxide reacted with benzene, with the formation of biphenyl and benzoic acid.

It is evident from the equation cited that for each mole of organometallic compound formed, one mole of CO_2 should be liberated. By measuring the rate of evolution of CO_2, we can judge the rate of the overall process. As is obvious from Curve 1 (Fig. 1), by expression of the relation of the quantity of CO_2 liberated to the logarithm of time, for the most part, the reaction proceeds according to an equation of the first order; without considering the initial and final stages of the process, the curve has a linear section.

An attempt to conduct the analogous reaction in cyclohexane was unsuccessful.

The reaction of acetyl peroxide with mercuric acetate proceeds by a different mechanism [3]. On conduction of the reaction at 80° in a benzene medium with an excess of mercury acetate, methylmercury acetate was obtained in a yield often exceeding 100% on conversion to the peroxide, and was equal to approximately 90% on the basis of the original mercury salt. Thus, obviously, a chain process occurs here. This reaction was investigated in the greatest detail. Since one molecule of CO_2 is also liberated for one molecule of methylmercury acetate formed here,

$$(CH_3CO_2)_2Hg \xrightarrow{\text{peroxide}} CO_2 + CH_3HgOCOCH_3,$$

this offers the possibility of observing the kinetics of the chain reaction very simply by the rate of liberation of the gas.

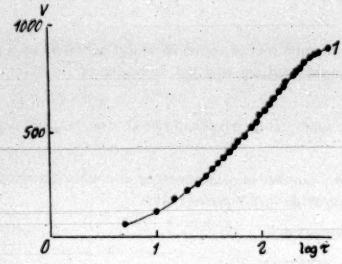


Fig. 1. Mercurous acetate and acetyl peroxide in benzene.

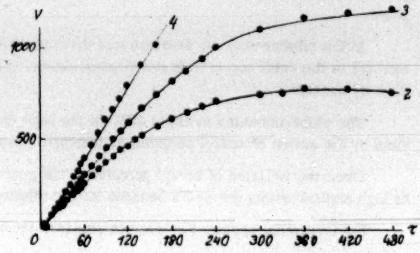


Fig. 2. Mercury acetate and acetyl peroxide in benzene. 2) 10.0 g of mercury acetate, 1.5 g of acetyl peroxide in 150 ml of benzene with 3.0 ml of acetic anhydride; 3) and 4) 20.0 g and 30.0 g of mercury acetate with proportions of the other components unchanged.

The experimental data obtained are presented by Curves 2-7 (Figs. 2 and 3), where the volumes of gas liberated, in milliliters converted to standard conditions, are plotted on the ordinate and the time in minutes is plotted on the abscissa. On each of these curves there is a linear section, for which the reaction rate is constant. At this stage, the reaction has a considerable excess of mercury acetate, and each methyl radical (primary or secondary) brings about the conversion of a molecule of mercury acetate. The reaction rate (the value of $\frac{\Delta V}{\Delta \tau}$) depends on the concentration of the starting materials, the peroxide and the mercury acetate. The reaction rate depends on the initial acetate concentration, which is evident from Fig. 2. The values of $\frac{\Delta V}{\Delta \tau}$ found for Curves 2, 3 and 4 were 4.06, 4.99 and 6.37, respectively. Thus, on change of the acetate concentration ratios of 1.0:2.0:3.0, the rates increased in the ratios of 1.0: 1.2: 1.6. The relation of the rate to the peroxide concentration is represented in Fig. 3, where $\frac{\Delta V}{\Delta \tau}$ for Curves 5, 6 and 7 was 4.99, 12.93 and 13.90. Consequently, by a 1.0:2.0:2.7 variation of the proportions of the peroxide concentration, the rate increased in the proportion of 1.0:2.6:2.8. It is evident from the data cited that the reaction rate exists in a rather complex relationship to the conditions of conduction of the reaction, and we did not succeed in showing any definite regularity. The length of the linear section of the curve increases with an increase of the initial quantities of mercury acetate and acetyl peroxide. The presence of acetic anhydride accelerates the reaction, although its role is not clear. When most of the mercury acetate has reacted, the linear course of the graph is disrupted. In this

case the propagation coefficient of the methyl radical is less than unity; it gradually decreases to zero; then not the process of propagation of the chain, but the process of breaking of the chain, begins. Because of these reactions, methane, methyl acetate and mercurous acetate form. The quantity of the latter decreases with an increase of the ratio of the quantity of peroxide to mercury acetate.

It is possible to accelerate the initiated decomposition reaction of mercury acetate by carrying it out in glacial acetic acid at 97-98°. In this case the yield of methylmercury acetate amounted to the theoretical quantity. At first the reaction proceeded very violently, and liberation of gas was so energetic that we were technically unable to record the kinetic curve. The reaction lasted for 1 hour all told, whereas in benzene solution it was completed after 7-8 hours.

The replacement of acetyl peroxide by other peroxides also enables us to initiate the decomposition of mercury acetate. However, on the basis of activating action they are surpassed by acetyl peroxide. Thus, for example, benzoyl peroxide, by action on mercury acetate in benzene, gave only a 54% yield of methylmercury acetate. The formation of this compound may be explained in this way.

$$CH_3COOHgOOCCH_3 + C_6H_5\cdot \text{ (from peroxide)} \longrightarrow \left[\begin{matrix} CH_3COOHgOOCCH_3 \\ C_6H_5\cdot \end{matrix}\right]^*$$

$$\left[\begin{matrix} CH_3COOHgOOCCH_3 \\ C_6H_5\cdot \end{matrix}\right]^* \longrightarrow CH_3COO\cdot + C_6H_5HgOOCCH_3$$

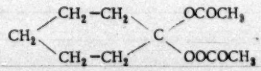
$$CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2$$

$$CH_3COOHgOOCCH_3 + CH_3\cdot \longrightarrow \left[\begin{matrix} CH_3COOHgOOCCH_3 \\ CH_3\cdot \end{matrix}\right]^*$$

$$\left[\begin{matrix} CH_3COOHgOOCCH_3 \\ CH_3\cdot \end{matrix}\right]^* \longrightarrow CH_3COO\cdot + CH_3HgOOCCH_3 \text{ etc.}$$

The yield of the phenyl derivative of mercury in this reaction amounted to 44.5%, on the basis of the benzoyl peroxide taken. Because of the reaction of benzoyl peroxide with benzene, besides the organometallic compounds of mercury, benzoic acid and biphenyl were formed. For benzoyl peroxide, just as in the presence of acetyl peroxide, a small quantity of mercurous salts formed.

As indicated above, in the catalytic decomposition reactions of mercury salts with acetyl peroxide, we used benzene solutions which contained a large quantity of acetic acid. The acetic acid could affect the reaction in a definite way; therefore, we wanted to carry out the reaction of the methyl-radical with mercury acetate in a solution which contained only benzene or only acetic acid. It seemed to us convenient to use the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide, which was easily obtained in the pure form [4], as the source of the methyl-radical.



On carrying out the reaction in benzene, the yield was much lower than with the initiator, acetyl peroxide. It should be noted that the reaction rate, determined for the linear portion of the curve $\Delta V/\Delta\tau$ equal to 6.4 ml/minute, differed little from the rate of the reaction initiated by acetyl peroxide. The presence of a linear section on Curve 8 (Fig. 4) indicates the chain character of the reaction with a propagation coefficient close to unity. The formation of a large quantity of mercurous salts should be noted.

On conduction of the reaction in acetic acid, we observed a great acceleration of the process. The reaction gave a negative result for Hg^{++} ion. The formation of a small quantity of mercurous salt was observed. There was a very large linear section on the kinetic curve (Fig. 5). Here the value of $\frac{\Delta V}{\Delta\tau}$ is equal to 160 ml/minute. Thus, the reaction rate in this experiment was 25 times greater than in the preceding experiment.

In order to show the generality of the present reaction for other mercuric salts of organic acids also, we studied the peroxide-initiated decomposition of mercuric salts of aliphatic and aromatic acids, propionic acid and benzoic acid. It was found that the decomposition of mercury propionate was also initiated by the peroxides. On carrying out the reaction in the presence of benzoyl peroxide in a benzene medium, we obtained the ethyl derivative of mercury in a 34% yield, on the basis of the salt used. Phenyl derivatives of mercury in high yields, on the basis of the peroxide, were also found in the reaction products. It can be assumed that the formation of both organometallic

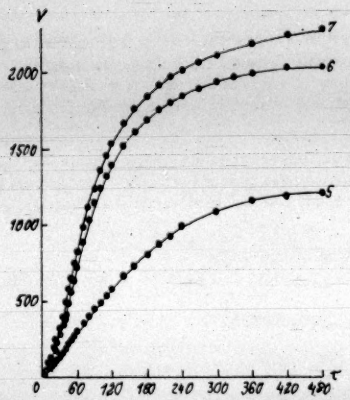


Fig. 3. Mercury acetate and acetyl peroxide in benzene. 5) 20.0 g of mercury acetate, 1.5 g of acetyl peroxide in 150 ml of benzene with 3.0 ml of acetic anhydride; 6) and 7) 3.0 and 4.0 g of acetyl peroxide with unvaried proportions of the other components.

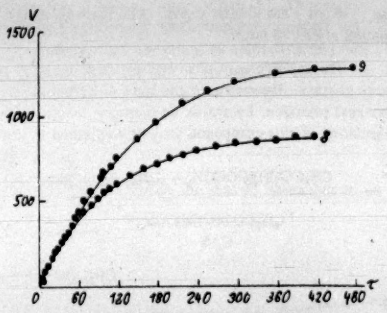


Fig. 4. 8) Mercury acetate and the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide in benzene; 9) mercury propionate and the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide in benzene.

compounds of mercury occurred analogously to the reaction of mercury acetate and benzoyl peroxide. In addition to these compounds, mercurous salts formed. The diacetylation derivative of 1-oxycyclohexyl-1-hydrogen peroxide also initiated the chain decomposition of bivalent mercury propionate. The kinetics of this reaction is represented by Curve 9 (Fig. 4), plotted on the same coordinates as was that for mercury acetate. A characteristic linear section on the curves, corresponding to a chain development stage, and confirming the chain mechanism of the process, is evident. The quantity $\frac{\Delta V}{\Delta \tau}$ was equal to 7.12 ml/minute, for this reaction is of the same order as the reaction of acetyl peroxide with mercury acetate. The formation of C_2H_5HgX was demonstrated.

Thus, the ethyl radical can bring about the chain decomposition reaction of mercury salts.

Unsatisfactory results were obtained with mercury benzoate. The mercury benzoate reacted chiefly with benzene on heating its benzene solution with benzoyl peroxide. The phenyl derivative of mercury was obtained in a very small quantity. A partial reduction of mercury benzoate to the mercurous salt and to metallic mercury was noted. The formation of metallic mercury in small quantities was also observed in the other experiments described.

EXPERIMENTAL

For the synthesis of acetyl peroxide we used a somewhat modified method of Smit [5], which was proposed for the synthesis of acetyl hydrogen peroxide. A solution of acetyl peroxide, which contained no acetyl hydrogen peroxide or free hydrogen peroxide was obtained by this method.

90.0 g of acetic anhydride and 2.0 g of sodium hydroxide were mixed carefully in a flask; the flask was cooled externally with snow and water. Later 18-20 g of 30% hydrogen peroxide was added. After addition of all the hydrogen peroxide, stirring and cooling were continued for 1 hour. The acetyl peroxide content was determined iodometrically. The solution contained no acetyl hydrogen peroxide nor unreacted hydrogen peroxide. There was 0.16-0.18 g of acetyl peroxide in 1 ml of the freshly-prepared solution. The acetyl peroxide solution could be used several days for the reaction; each day before the experiment the quantity of peroxide in the solution was determined.

Reaction of the peroxide with mercury salts was carried out in a three-necked flask to which a stirrer, thermometer and reflux condenser were connected in sections; two gas burettes, for measuring the volume of gasses

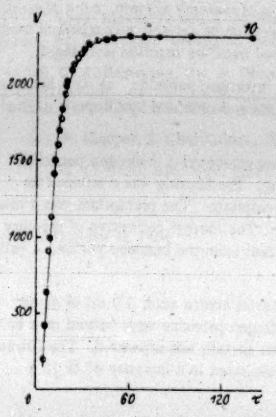


Fig. 5. Mercury acetate and the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide in acetic acid.

which formed during the reaction, were connected to the reflux condenser. Methylmercury acetate formed in the majority of the experiments. Methylmercury acetate was a more volatile substance which was quite highly soluble in acetic acid and water, and its quantitative separation presented great difficulty; therefore, the most convenient method found for the determination of the methylmercury acetate was the precipitation of methylmercury iodide by means of NaI or KI. The methylmercury iodide was much more difficultly soluble, crystallized well, and was easily obtained in the pure form. Precipitation as methyl mercurous chloride gave lowered results, because of its greater solubility and volatility. The melting points of the organomercury compounds obtained were verified each time by a test sample of a mixture with the pure preparation.

1. Reaction of Mercurous Salts with Peroxides

Mercurous acetate and acetyl peroxide in a solution of benzene. 15.0 g of mercurous acetate, 18 ml of a solution containing 3.25 g of acetyl peroxide, and 150 ml of benzene were heated 7.5 hours at the boiling point of benzene. The benzene solution was filtered off from the precipitate and repeatedly extracted with water. By addition of potassium iodide to the aqueous extract, methylmercurous iodide formed in a quantity of 9.3 g (49%, on the basis of the initial peroxide). The m.p. was 145°.

Mercurous acetate and benzoyl peroxide in a benzene solution. 8.0 g of mercurous acetate, 3.0 g of benzoyl peroxide purified by precipitation with methanol from a chloroform solution, and 60 ml of benzene were heated at the boiling point of benzene for 11.5 hours. On completion of the reaction, the solution was separated from the excess mercurous acetate and distilled on the water bath. A saturated aqueous solution of $CaCl_2$ was added to the material remaining from the distillation and steam was passed in. The residue from the steam-distillation was filtered off and recrystallized from acetone. 2.25 g of phenylmercurous chloride (29% based on the initial benzoyl peroxide), with a m.p. of 255°, was formed. 0.25 g of benzoic acid with a m.p. of 120° (from water) was formed by addition of a mineral acid to the filtrate. 0.4 g of biphenyl with a m.p. of 67° was collected in the distillate.

2. Reactions of Mercuric Salts with Peroxides

Mercury acetate and acetyl peroxide. a) In a benzene solution. 40.0 g of mercury acetate and 25 ml of a solution containing 3.8 g of acetyl peroxide and 70 ml of benzene were heated for 9 hours. The white suspension, after about 2 hours, was converted to a clear, dark-yellow solution. On completion of the reaction, the solution was separated from the small quantity of metallic mercury. The filtrate was extracted with water, and from it, by addition of potassium iodide, methylmercury iodide with a m.p. of 144° was precipitated in a quantity of 38.5 g (89.5% on the basis of mercury acetate).

A series of similar syntheses was carried out with variable quantities of reaction components, in which the formation of mercurous salts and methyl acetate in varying quantities was observed. Thus, 2.25 g of mercurous acetate was obtained from 10.0 g of mercury acetate, 1.5 g of acetyl peroxide (8.0 ml of solution) and 150 ml of benzene. In another experiment, where 20.0 g of mercury acetate, 3.0 ml of acetic anhydride, 3.5 g of acetyl peroxide and 150 ml of benzene were used, the solution was distilled at 79°. 40 ml of 0.5 N alcohol-water alkali was added to the distillate. The mixture was refluxed on the water bath for 4.5 hours. Then water was added and the quantity of alkali consumed by saponification was determined by titration. The methyl acetate content found was 0.73 g. The carbon dioxide gas liberated contained a small quantity of methane.

b) In an acetic acid solution. 58.8 g of mercury acetate, 230 ml of glacial acetic acid, 3.0 ml of acetic anhydride and 2.0 g of acetyl peroxide were heated for 1 hour. At first the evolution of gas proceeded very energetically, then it quickly ceased. On completion of the heating, the reaction mass was diluted with water (by 2-3 times) and methylmercury iodide was precipitated in a quantity of 62.8 g (99% on the basis of mercury acetate) by sodium iodide. From the acetate solutions thus obtained, by careful evaporation of the reaction mixture, we were able to

obtain methylmercury acetate, which after purification by sublimation had a m.p. of 128°.

On conducting this experiment in a solution of dilute acetic acid (20.0 g of mercury acetate, 3.0 g of acetic anhydride, 50 ml of acid, 100 ml of water and 2.0 g of acetyl peroxide) a slight liberation of gas and only traces of methylmercury compounds were observed. Most of the mercury acetate was recovered from the reaction unchanged.

Mercury acetate and the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide. a) In a benzene solution. The diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide was obtained by Cooper's method [4]; the m.p. was 72°.

15.0 g of mercury acetate, 2.5 g of the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide, and 150 ml of benzene were heated on the water bath with stirring and boiling. The heating was continued for 7 hours. On completion of the reaction, the solution was separated from the precipitate. The precipitate was a mixture of mercuric salts, which contained mercurous salts; the weight was 5.5 g. The methyl derivative of mercury in a yield of 40.4% was separated in the usual way. After removal of the solvent from the benzene portion, a yellow oil remained, which was not investigated closely.

b) In an acetic acid solution. 29.9 g of mercury acetate, 90 ml of glacial acetic acid, 3.0 ml of acetic anhydride and 3.0 g of the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide were heated on a boiling water bath for 1 hour. On completion of the reaction, 0.45 g of mercurous acetate was separated. The filtrate was diluted (by 2-3 times) with water and methylmercurous chloride was precipitated in a quantity of 18.15 g (78.3% on the basis of mercury acetate) by the action of KCl.

Mercury acetate and benzoyl peroxide in benzene. 15.0 g of mercury acetate, 3.0 g of benzoyl peroxide and 60 ml of benzene were heated on the water bath at the boiling point of benzene for 12 hours. On completion of the reaction, the solution was filtered from the precipitate. The precipitate contained Hg^{++} and Hg_2^{++} ions, but was not investigated closely; its weight was 2.3 g. The filtrate was extracted with water, sodium iodide was added to the aqueous portion, and 8.75 g (54% on the basis of mercury acetate) of methylmercury iodide with a m.p. of 142° was obtained. After washing with water, the benzene portion was distilled. After removal of the benzene, a saturated solution of $CaCl_2$ was added to the residue and steam was passed in. From the residue after steam-distillation 3.24 g (41.7% on the basis of benzoyl peroxide) of phenylmercurous chloride with a m.p. of 250° (from acetone) was obtained. After acidification, 0.15 g of benzoic acid, m.p. of 120°, was obtained. From the distillation 0.2 g of biphenyl with a m.p. of 67° was separated.

Mercury benzoate and benzoyl peroxide in benzene solution. 7.2 g of mercury benzoate, 2.0 g of benzoyl peroxide and 60 ml of benzene were heated for 12 hours. After completion of the reaction, 2.1 g of mercury benzoate was filtered off (drops of metallic mercury were observed). The filtrate was distilled, a saturated solution of $CaCl_2$ was added to the residue and steam was passed in. From the residue after steam-distillation, 2.9 g of a mixture of calomel and a small quantity of phenylmercurous chloridewere formed; the latter after two recrystallizations from acetone had a m.p. of 257°. Among the other products, 1.45 g of benzoic acid with a m.p. of 122°, and 0.45 g of biphenyl, were obtained.

Mercury propionate and benzoyl peroxide in a benzene solution. 15.0 g of mercury propionate, 2.0 g of benzoyl peroxide and 60 ml of benzene were heated for 12 hours. After completion of the reaction, 60 ml of benzene were heated for 12 hours. After completion of the reaction, 0.6 g of mercurous propionate was filtered off. The filtrate was extracted with water and potassium chloride was added to the aqueous portion. Thus, 1.95 g of ethylmercurous chloride with a m.p. of 193° was obtained. After separation of the ethylmercurous chloride, sodium iodide was added to the aqueous portion; thus, 1.65 g of ethylmercurous iodide, m.p. 180° (with decomposition), was obtained. The benzene solution was distilled. KCl was added to the residue and steam was passed in. From the residue after the steam-distillation, 5.4 g of a mixture containing phenylmercurous chloride and calomel was obtained. On extraction with acetone, and after two recrystallizations from it the phenylmercurous chloride had a m.p. of 258°. From the steam distillate 0.7 g more of ethylmercurous chloride was separated. Thus, the total yield of C_2H_5HgX amounted to 34% of the theoretical, on the basis of the initial mercury propionate. Moreover, 0.9 g of benzoic acid was obtained in the experiment.

SUMMARY

1. A new method for the synthesis of organomercury compounds of the aliphatic series, based on the reaction of mercuric salts of aliphatic acids with peroxide, was presented.

2. It was shown that chain reactions take place with the action of acetyl peroxide, benzoyl peroxide and the diacetylated derivative of 1-oxycyclohexyl-1-hydrogen peroxide on mercury acetate and mercury propionate. A chain radical mechanism was proposed for the process.

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REACTION OF DI-p-METHOXYPHENYLMERCURY WITH PHENOLS. X.

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It was shown earlier [1] that diphenylmercury, and also some other aromatic mercury derivatives (dinaphthylmercury, ditolylmercury, dibenzylmercury) [2], have the capacity to mercurize phenols, with the formation of the mono-, di- and trimercurized derivatives; moreover, the nature of the substituent entering into the composition of the benzene ring of the organomercury compound plays an essential role. It was of interest to study the mercurization reactions by means of di-p-methoxyphenylmercury, a thermally stable compound [3]. The reaction of the interaction of di-p-methoxyphenylmercury with the following phenols was studied: p-nitrophenyl, o-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, resorcinol, p-cresol and phenol. The reaction was studied in the absence of solvents and in a temperature range of 70-130°.

With phenols, di p-methoxyphenylmercury forms chiefly the mono- and dimercurized derivatives as crystalline substances. The monomercurized derivatives have sharp melting points and are soluble in organic solvents (alcohol and benzene). The dimercurized derivatives are infusible and insoluble (except solutions of alkalies). The formation of anisole was observed in all cases.

$$(p\text{-}CH_3OC_6H_4)_2Hg + RC_6H_4OH \longrightarrow p\text{-}CH_3OC_6H_4HgC_6H_3(OH)R + CH_3OC_6H_5$$

$$2(p\text{-}CH_3OC_6H_4)_2Hg + RC_6H_4OH \longrightarrow (p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)R + 2CH_3OC_6H_5$$

On heating di-p-methoxyphenylmercury with unsubstituted phenols (3 hours at 130°), we observed the formation of metallic mercury, the quantity of which increased in the following order: phenol 5.63%, resorcinol 41.07%, hydroquinone 52.20%, pyrogallol 76.43%.

EXPERIMENTAL

All the experiments were carried out in sealed glass ampoules, which were heated in an oil thermostat. We used 0.2 g of phenols to 0.2 g of di-p-methoxyphenylmercury. After the heating, anisole (according to Sivolobov, b.p. 153-154°) separated from the reaction mixture, and the monomercurized derivative was removed by treatment with alcohol or benzene. The insoluble residue was a dimercurized derivative, which sometimes contained metallic mercury, the quantity of which was determined by the usual methods.

Di-p-Methoxyphenylmercury and o-Nitrophenol

Experiment 1: 100°, 3 hours. Fine, bright-orange crystals (0.12 g) of the monomercurized derivative, with a m.p. of 109-110°, were separated from a benzene solution.

0.0300 g sub.: 1.35 ml 0.1 N NH_4CNS. Found %: Hg 45.00. $p\text{-}CH_3OC_6H_4HgC_6H_3(OH)NO_2$. Calculated %: Hg 45.07.

Experiment 2: 130°, 3 hours. 0.14 g of the bright-yellow crystals (insoluble and infusible up to 250°) of the dimercurized derivative was obtained.

0.0300 g sub.: 1.61 ml 0.1 N NH_4CNS. Found %: Hg 53.67. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 53.47.

The structure of the monomercurized derivative was demonstrated as follows. By treatment with an alcoholic solution of HCl, the formation of anisole, mercuric chloride and o-nitrophenol was observed. 2-Nitro-4-bromophenol was formed as yellow needles with a m.p. of 89° (test sample of mixture 89°) by the action of bromine in a saturated solution of potassium bromide. Consequently, the monomercurized compound was 2-nitro-4-p-methoxyphenylmercury-1-hydroxybenzene.

Di-p-Methoxyphenylmercury and p-Nitrophenol

The insoluble, infusible, yellow, finely crystalline precipitate of the dimercurized derivative (0.24 g) was formed by heating at 130° for 3 hours.

0.0500 g sub.: 2.64 ml 0.1 N NH_4CNS. Found %: Hg 52.80. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)NO_2$. Calculated %: Hg 53.48.

Di-p-Methoxyphenylmercury and 2,4-Dinitrophenol

The insoluble, infusible, orange-colored, finely-crystalline precipitate of the dimercurized derivative (0.1 g) was formed by a 3-hour heating at 130°.

0.05 g sub.: 2.63 ml 0.1 N NH_4CNS. Found %: Hg 52.60. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H(OH)(NO_2)_2$. Calculated %: Hg 52.40.

In addition, 3.55% of metallic mercury was obtained.

Di-p-Methoxyphenylmercury and 2,4,6-Trinitrophenol

The yellow crystalline precipitate of the monomercurized derivative (0.13 g) with a m.p. of 125-126°, was formed after 3 hours at 100°.

0.05 g sub.: 1.91 ml 0.1 N NH_4CNS. Found %: Hg 38.20. $p\text{-}CH_3OC_6H_4HgC_6H(OH)(NO_2)_3$. Calculated %: Hg 38.65.

Di-p-Methoxyphenylmercury and p-Chlorophenol

The monomercurized derivative (0.09 g) was obtained as white crystals with a m.p. of 154-156° by carrying out the reaction at 70° for 3 hours.

0.05 g sub.: 2.39 ml 0.1 N NH_4CNS. Found %: Hg 47.80. $p\text{-}CH_3OC_6H_4HgC_6H_3(OH)Cl$. Calculated %: Hg 47.68.

The dimercurized derivative was obtained after 3 hours at 100° as coarse white crystals (0.15 g), which were insoluble and infusible.

0.05 g sub.: 2.72 ml 0.1 N NH_4CNS. Found %: Hg 54.40. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)Cl$. Calculated %: Hg 54.16.

Di-p-Methoxyphenylmercury and 2,4,6-Trichlorophenol

The monomercurized derivative formed as white crystals (0.25 g) with a m.p. of 178-181°, after 3 hours at 70°.

0.05 g sub.: 1.88 ml 0.1 N NH_4CNS. Found %: Hg 37.60. $p\text{-}CH_3OC_6H_4HgC_6H(OH)Cl_3$. Calculated %: Hg 38.32.

After 3 hours at 100°, 0.06 g of the alcohol-soluble monomercurized derivative with a m.p. of 179-181° and 0.15 g of the dimercurized derivative as insoluble and infusible fine, white crystals formed.

0.05 g sub.: 2.44 ml 0.1 N NH_4CNS. Found %: Hg 48.80. $(p\text{-}CH_3OC_6H_4Hg)_2C_6(OH)Cl_3$. Calculated %: Hg 48.63.

Only the dimercurized derivative formed after 3 hours at 130°.

Di-p-Methoxyphenylmercury and Resorcinol

On heating the reaction mixture for 3 hours at 100°, the monomercurized derivative (0.1 g) was separated from an alcoholic solution as orange crystals with a m.p. of 169-170°.

0.05 g sub.: 2.43 ml 0.1 N NH_4CNS. Found %: Hg 48.60. $p\text{-}CH_3OC_6H_4HgC_6H_3(OH)_2$. Calculated %: Hg 48.15.

The insoluble trimercurized derivative precipitate consisted of infusible, insoluble fine yellow crystals (0.2 g).

0.05 g sub.: 2.95 ml 0.1 N NH_4CNS. Found %: Hg 59.00. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H(OH)_2$. Calculated %: Hg 58.64.

Only the formation of metallic mercury was observed on heating the reaction mixture at 130°.

Di-p-Methoxyphenylmercury and p-Cresol

The dimercurized derivative separated as insoluble and infusible white crystals on heating the reaction mixture at 70 and 100° (3 hours).

0.05 g sub.: 2.51 ml 0.1 N NH_4CNS. Found %: Hg 50.20. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)CH_3$. Calculated %: Hg 55.64.

On heating the reaction mixture at 130°, only the formation of metallic mercury was observed.

Di-p-Methoxyphenylmercury and Phenol

The formation of the dimercurized derivative as colorless crystals in a quantity of 0.12 g was observed after 3 hours at 70°.

0.05 g sub.: 3 ml 0.1 N NH_4CNS. Found %: Hg 60.00. $(p\text{-}CH_3OC_6H_4Hg)_2C_6H_3(OH)$. Calculated %: Hg 56.73.

SUMMARY

1. It was shown that di-p-methoxyphenylmercury has the capacity to mercurize phenols, with the formation of the mono- and dimercurized derivatives.

2. The rate of the reaction of phenols with di-p-methoxyphenylmercury depends on the nature, mutual arrangement and number of substituted groups in the benzene ring of phenol.

LITERATURE CITED

[1] M. M. Koton and T. M. Zorina, J. Gen. Chem., 17, 1220 (1947).

[2] M. M. Koton, J. Gen. Chem., 20, 2096 (1950);* M. M. Koton and I. A. Chernov, J. Gen. Chem., 19, 2104 (1949).**

[3] M. M. Koton and V. F. Martynova, J. Gen. Chem., 24, 2177 (1954).

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* See Consultants Bureau Translation, page 2171.

** See Consultants Bureau Translation, page a-575.

α-KETO OXIDES AND THEIR TRANSFORMATIONS. IV. THE OXIDES OF 2-METHYL-1,4-HEXADIEN 3-ONE, 5-METHOXY-2-METHYL-1-HEXEN 3-ONE AND 1-METHOXY-2-METHYL-4-HEXEN -3-ONE

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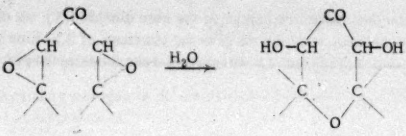
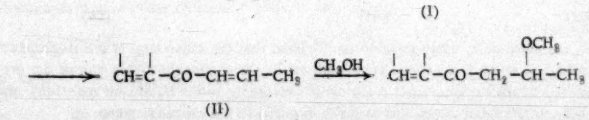
In one of the previous reports [1] it was shown that, by the action of alkaline hydrogen peroxide on divinyl ketones, the corresponding keto dioxides form smoothly in a yield of up to 70%:

The hydrolysis reaction of the keto dioxides and their reaction with the amines, as a result of which hydroxylated heterocyclic ketones are formed, proved to be especially interesting:



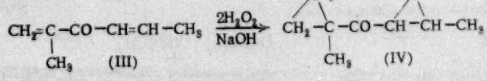
It was of interest to investigate the oxidation reaction of the dienones and of their corresponding unsaturated β-methoxy ketones, which are easily obtained via the hydration of the divinylacetylene hydrocarbons in aqueous solutions of methanol, in the presence of mercury sulfate, by a general method developed in our laboratory [3]:



In the first stages of the hydration reaction of the divinyl acetylene hydrocarbons there is the formation of vinyl allyl ketones (I), which under the conditions of the experiment (under the influence of mercury sulfate and elevated temperature) are easily isomerized to the more stable vinyl propenyl ketones (II), with a system of conjugated double bonds. A similar type of isomerization of the allyl ketones to the corresponding propenyl ketones under the influence of acids, alkalies, and other agents has already been described in the literature [4].

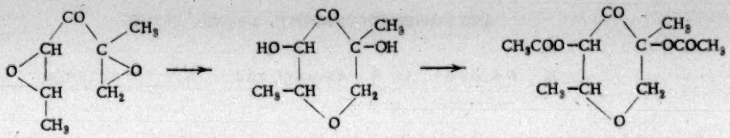
We studied the reaction of alkaline hydrogen peroxide with readily available propenyl isopropenyl ketone (III) and unsaturated methoxy ketones (X) and (XXIII), which were formed as a result of the addition of methanol to propenyl isopropenyl ketone [3].

It was found that propenyl isopropenyl ketone (III) was readily oxidized, by the action of alkaline hydrogen peroxide in a solution of dioxan. to the keto dioxide (IV) with a yield of 64%:



The result obtained was found to be in agreement with our previous works [1], and also with the indications of Weitz and Scheffer [2], and Reese [2a], concerning the fact that the oxidation by alkaline hydrogen peroxide has a strictly selective character and takes place smoothly only in those cases when the double bonds are found to be in a conjugated position to the carbonyl group.

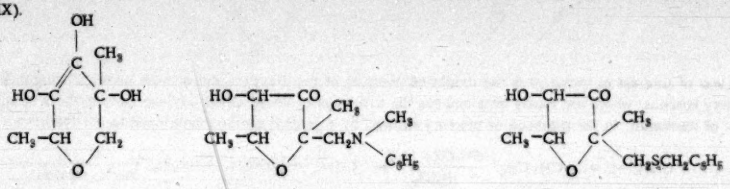
On dissolving the keto dioxide (IV) in water at room temperature, it slowly underwent hydrolysis and was converted to 2,5-dimethyl-3,5-dihydroxytetrahydro-4-pyrone (V), which formed the diacetate (VI) by the action of acetic anhydride:



(IV) (V) (VI)

The hydrolysis of the keto dioxide (IV) at elevated temperature takes place much more rapidly, but in addition to this, the yield of crystalline dihydroxypyrone (V) decreases and the yield of its syrupy isomeric product increases. The liquid isomer has an increased hydroxyl group content, and on standing is slowly converted to the crystalline dihydroxypyrone (V), does not form a crystalline carbonyl group derivative, gives the diacetate (VI) by the action of acetic anhydride; the presence of an unsaturated bond was observed; the isomer was soluble in water and in alcohol, it was vacuum distilled and was, in all probability, the enolic triol of the pyran structure (VII).

By the action of methylaniline and benzylmercaptan on the keto dioxide (IV), we obtained in a yield of 33-57% the corresponding heterocyclic ketones, to which we gave the structures of 2,5-dimethyl-2-methylphenylaminomethyl-4-hydroxytetrahydrofuran-3-one (VIII) and 2,5-dimethyl-2-benzylmercaptomethyl-4-hydroxytetrahydrofuran-3-one (IX).

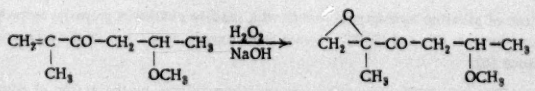


(VII) (VIII) (IX)

This structure was assumed as most probable on the basis that the oxide ring of the isopropenyl group, which contained a tertiary carbon atom in the ring, opens more readily than does the oxide ring of the propenyl group, which contained two secondary carbon atoms in the cycle (according to the hydrolysis reaction), and the radicals of the amines and benzylmercaptan should add to the β-position to the carbonyl group.

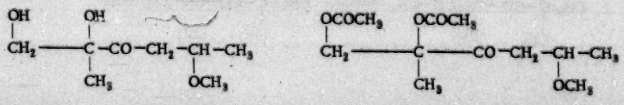
We were unable to form the corresponding heterocyclic amino ketones by the action of ethylamine and diethylamine on the keto dioxide (IV), because of the almost complete resinification of the reaction products.

By the action of alkaline hydrogen peroxide on 5-methoxy-2-methyl-1-hexen-3-one (X) in a solution of methanol, a 67% yield of the keto oxide (XI) formed:



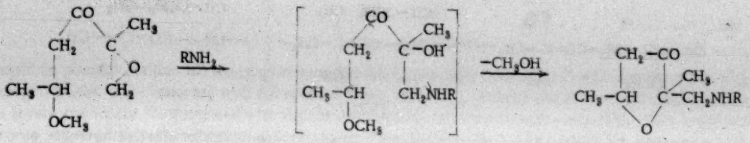
(X) (XI)

On heating with water, the keto oxide (XI) was hydrolyzed to the keto glycol (XII), which by the action of acetic anhydride was converted to the diacetate (XIII):



(XII) (XIII)

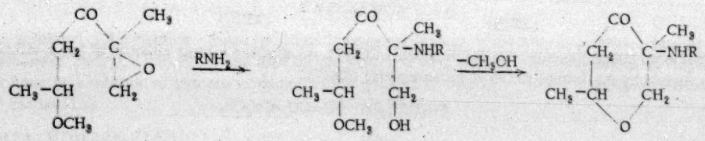
It was shown earlier by our laboratory [5, 6] that on reaction of ammonia and primary amines with vinyl propenyl ketones and their methanol addition products, various γ-piperidones are formed very smoothly. Thanks to the presence of the oxide ring and the methoxy group, the keto oxide (XI) under mild conditions condenses with the primary amines, forming a yield of up to 50% of the cyclic amino ketones (with a secondary nitrogen atom), which, in all probability, have the furan structures (XIV), (XV), (XVI):



(XI)

(XIV) R = C_6H_5,
(XV) R = C_2H_5,
(XVI) R = CH_3.

However, the possibility is not excluded of the formation in addition of amino ketones of the pyran structure according to the following scheme:

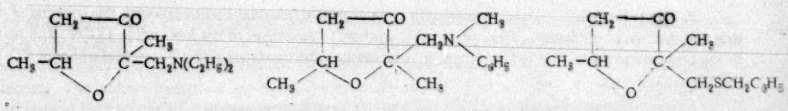


(XI)

The presence of a secondary nitrogen in the compounds (XIV), (XV) and (XVI) was shown by acetylation reactions and by the formation of nitrosamines.

The condensation reaction of the keto oxide (XI) with secondary amines takes place especially smoothly. By heating this keto oxide with diethylamine and methylaniline in a sealed ampoule, we obtained 2,5-dimethyl-2-diethylaminomethyltetrahydrofuran-3-one (XVII) and 2,5-dimethyl-2-methylphenylaminomethyltetrahydrofuran-3-one (XVIII) in a yield of 63-65%.

By a similar method, the keto oxide (XI), by reaction with benzylmercaptan, formed 2,5-dimethyl-2-benzylmercaptomethyltetrahydrofuran-3-one (XIX) in a yield of 50% [7, 8].



(XVII) (XVIII) (XIX)

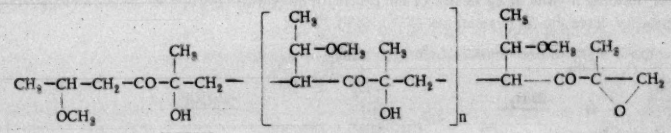
By Kötz it was shown [9] that some α-keto oxides, like the oxides of the olefins [10] and the glycidic ethers [11], promote condensation on rupture of the oxide ring by sodium-malonic and sodium-acetoacetic esters, with the formation of lactones. By condensation of the keto oxide (XI) with the sodium-malonic and sodium-acetoacetic esters, in a solution of anhydrous alcohol in the presence of sodium ethylate, the corresponding lactones (XX) and (XXI) were obtained in a small yield:

(XX)

(XXI)

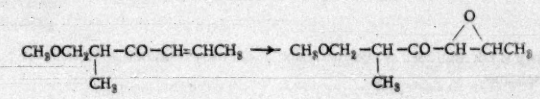
On storage of the keto oxide (XI) for about a year, it thickened greatly, and on addition of this product to water the solid, amorphous polymer with an average molecular weight corresponding to 14 elementary particles.

precipitated. The presence of hydroxyl groups was detected in the polymer according to Tserevitinov. The formation of the polymer probably occurs because of the intermolecular transference of the α-hydrogen atom of the methylene group of one molecule to the oxide ring of a second molecule, and has the structure (XXII):



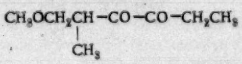
(XXII)

The oxidation reaction of 1-methoxy-2-methyl-4-hexen - 3-one (XXII) by alkaline hydrogen peroxide in a solution of methanol proceeded smoothly, and moreover, the keto oxide (XXIV) formed in a yield of 76%:



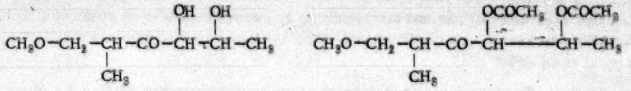
(XXIII) (XXIV)

In this experiment, together with the keto oxide (XXIV), we obtained a large quantity of the α-diketone (XXV), which was formed by the isomerization of the keto oxide (XXIV).



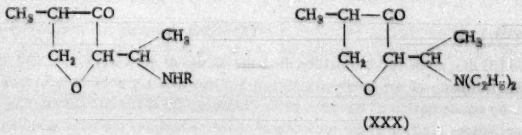
(XXV)

By prolonged heating of the keto oxide (XXIV) with water, or better in the presence of acid, it was hydrolyzed to the keto glycol (XXVI), which by the action of acetic anhydride formed the diacetate (XXVII):



(XXVI) (XXVII)

The keto oxide (XXIV) also entered into a condensation reaction connected with the opening of the oxide ring and the loss of methanol. Thus, on heating equimolar quantities of the keto oxide (XXIV) and primary amines in the presence of water in a sealed ampoule, we obtained the corresponding alkylaminofuranones (XXVIII) and (XXIX).

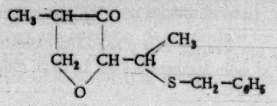


(XXX)

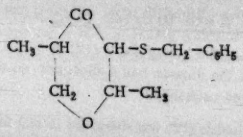
(XXVIII) R= C_2H_5, yield 46%.
(XXIX) R= C_6H_5, yield 20%.

The reaction of the keto oxide (XXIV) with diethylamine, which took place on heating the components in a sealed ampoule in the presence of alcohol, led to the formation of a 40% yield of 2-(α-diethylamino)-ethyl-4-methyltetrahydro-3-furanone (XXX).

By the action of benzylmercaptan on the keto oxide (XXIV), on heating we obtained two isomeric substances: a crystalline substance with a yield of 15%, and a liquid substance with a yield of 69%, which were possibly geometric isomers of 4-methyl-2-(α-benzylmercapto)-ethyltetrahydrofuran-3-one (XXXI). It was not excluded, however, that the compounds obtained might have the pyran structure (XXXII):



(XXXI)



(XXXII)

It should be pointed out that all the reactions carried out for the keto oxide (XXIV) with compounds having mobile hydrogen atoms, and connected with the opening of the oxide ring, proceed much more difficultly and require more severe conditions, as compared with similar reactions for its isomeric keto oxide (XI). This is explained by the presence of two secondary carbon atoms in the ring of the oxide (XXIV), in contrast to the keto oxide (XI), which has a tertiary carbon atom in the oxide ring, which agrees with the data of Eltekov [12] for the olefin oxides.

Thus, the above-described condensation reaction of the α-keto oxides offers the possibility of easily synthesizing various new, formerly completely unavailable derivatives of the tetrahydropyran or furan series on the basis of acetylene.

EXPERIMENTAL

The 2-methyl-1,4-hexadien-3-one (propenyl isopropenyl ketone), 5-methoxy-2-methyl-1-hexene-3-one and 1-methoxy-2-methyl-4-hexen-3-one used for the oxidation were obtained by the hydration of vinylisopropenylacetylene in a solution of aqueous methanol, in the presence of mercury sulfate and sulfuric acid, by a method described earlier [13].

The Keto Dioxide (IV)

Into a 3.5 liter, three-necked flask, equipped with a thermometer, mechanical stirrer and two dropping funnels, we introduced 230 g of propenyl isopropenyl ketone (III) (b.p. 43-45° at 10 mm, n_D^{18} 1.4712), diluted with 1.5 liters of dioxan. To the solution cooled to −5°, with energetic mixing, during 2 hours, we added simultaneously from the two dropping funnels 830 ml (2 moles) of 18% solution of hydrogen peroxide and 85 ml of a 4 N aqueous solution of sodium hydroxide. The oxidation reaction took place very energetically; addition of the first portions of hydrogen peroxide and alkali caused a sharp increase of the temperature. The temperature of the reaction mixture was maintained not above +5°, which was achieved by cooling the reaction flask with a mixture of ground ice and salt and by a slow rate of addition of the alkaline hydrogen peroxide. After introduction of hydrogen peroxide, the reaction flask was removed from the cooling bath and allowed to stand for some time at room temperature, care being taken that the temperature of the reaction mixture did not rise above 20-25°.

1.5 hours after introduction of the oxidizing agent into the reaction mixture, about 7 g of hydrogen peroxide remained, which corresponded to the excess of the latter which was introduced. The original light-yellow solution, moreoever, was completely decolorized and lost its sharp epiphora-producing odor which was native to propenyl isopropenyl ketone. The sodium hydroxide was neutralized by 10% sulfuric acid, and the rest of the hydrogen peroxide was decomposed by addition of manganese dioxide to the reaction mixture. The sodium sulfate which deposited was removed by filtration, the solvent and the major portion of the water were removed in vacuo (before the separation), the product was extracted three times with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. As a result of three vacuum distillations 151 g of the keto dioxide (IV) was obtained as a colorless, almost odorless liquid.

B.p. 93° (5 mm), 79° (1 mm), n_D^{20} 1.4510, d_4^{20} 1.1166, MR 34.30; calculated 34.80.

Found %: C 58.84, 58.97; H 7.29, 7.32. M 140.4, 140 (in benzene). $C_7H_{10}O_3$. Calculated %: C 59.15; H 7.05, M 142.

The 2,4-dinitrophenylhydrazone consisted of fine, acicular crystals with a m.p. of 224-226° (after washing on the filter with methanol). We were unable to recrystallize it, since it did not precipitate from solution, even from the smallest quantities of solvent.

Found %: N 18.16, 18.24. $C_{13}H_{14}O_6N_4$. Calculated %: N 17.73.

The keto dioxide (IV) was soluble in water and in the usual organic solvents.

Hydrolysis of the Keto Dioxide (IV)

a) The hydrolysis of the keto dioxide (IV) by water at room temperature took place rather slowly. Only 1/3 of an aqueous solution of the dioxide had hydrolyzed on standing at room temperature for 14 days, and the remaining quantity was recovered unchanged.

20 g of the keto dioxide (IV) was dissolved in 180 ml of distilled water and allowed to stand at room temperature for 45 days. After removal of the water in vacuo at a bath temperature of 30-35°, 26 g of a light-yellow, viscous syrup was obtained in the residue. On prolonged standing in a vacuum-desiccator over phosphoric anhydride, it was converted to a semi-liquid mass (paste), which consisted of a mixture of the fine crystals and the viscous liquid substance. The mixture was diluted with dry chloroform, the crystalline portion was removed by filtration at low vacuum, washed with chloroform and recrystallized from dioxan. We obtained 4.5 g of 2,5-dimethyl-3,5-dihydroxytetrahydro-4-pyrone (V) as fine, colorless, prismatic crystals with a m.p. of 167° (in a sealed capillary) and a sublimation temperature of 212-215° at 0.5 mm.

Found %: C 52.15, 52.28; H 7.56, 7.43. M 161, 164 (according to Rast). $C_7H_{12}O_4$. Calculated %: C 52.52; H 7.50. M 160.

Found %: OH 22.10, 21.57 (in pyridine). $C_7H_{10}O_2(OH)_2$. Calculated %: OH 21.25.

The semicarbazone consisted of colorless, acicular crystals with a m.p. of 218-219° (from water).

Found %: N 19.63, 19.16. $C_8H_{15}O_4N_3$. Calculated %: N 19.36.

The dihydroxypyrone (V) was highly soluble in pyridine, more difficultly soluble in water and alcohol, and insoluble in ether, benzene and chloroform. It crystallized from dioxan and ethanol as characteristic fine, prismatic crystals.

After removal of the chloroform the liquid portion was vacuum distilled. 9.5 g of an almost colorless, viscous syrup was obtained, which was probably a mixture of the dihydroxypyrone (V) and its enolic form (VII).

B.p. 117-119° (3 mm), n_D^{20} 1.4785, d_4^{20} 1.2137, MR 37.37; calculated 38.08 for trihydroxypyran (VII) and 37.03 for dihydroxypyrone (V).

Found %: C 52.21, 52.69; H 7.65, 7.13; OH 24.29, 23.26. $C_7H_{10}O_2(OH)_2$. Calculated %: C 52.50, H 7.50; OH 21.25.

The liquid product was soluble in water and in alcohol, and insoluble in ether and benzene. In acidic solutions it liberated iodine from potassium iodide, but it did not form crystalline derivatives with phenylhydrazine and semicarbazide. On standing, it slowly crystallized to the above-described crystalline dihydroxypyrone (V) with a m.p. of 167°.

b) 25 g of the keto dioxide (IV), dissolved in 200 ml of distilled water, was heated on a boiling water bath for 30 hours. At this time the colorless solution became a light-yellow color. After removal of the water in vacuo at a bath temperature of 32-34°, we obtained in the residue 27.5 g of a light yellow, neutral, viscous syrup which was vacuum distilled (3 mm):

1st fraction b.p. 83-109°, n_D^{18} 1.4645, 1 g; 2nd fraction, b.p. 109-115°, n_D^{18} 1.4798, 8 g; 3rd fraction, b.p. 115-123°, n_D^{18} 1.4810, 12.5 g.

The orange-colored residue (about 5 g), did not distill at the bath temperature of 170° (3 mm).

The 1st fraction was chiefly the original keto dioxide. On standing, fine crystals came down in the 2nd and 3rd fractions. After 3 weeks both of the latter fractions were combined, and diluted with anhydrous chloroform; the crystalline product which came down was separated by filtration, washed with chloroform and recrystallized from dioxan. We obtained 2.3 g of the crystalline dihydroxypyrone (V) with a m.p. of 167°, which gave no m.p. depression with the above-described form.

Found %: C 52.30; H 7.69. $C_7H_{12}O_4$. Calculated %: C 52.50, H 7.50.

After evaporation of the chloroform in vacuo the liquid product was vacuum distilled. 10 g of an almost colorless syrup, with a b.p. of 117-119° at 3 mm, was separated, which, judging by the hydroxyl group content, was chiefly trihydroxydihydropyran (VII).

Found %: C 52.07, 52.38; H 7.65, 7.31; OH 33.78, 33.42 (in pyridine). M 164, 162 (in dioxan). $C_7H_9O(OH)_3$. Calculated %: C 52.50, H 7.50; OH 31.87. M 160.

Trihydroxypyran (VII) was soluble in water, alcohol and pyridine, more difficultly soluble in chloroform, and insoluble in ether and benzene. It decolorized bromine water and a permanganate solution, and liberated iodine from an acid solution of potassium iodide. It did not form carbonyl group derivatives. On standing, it was very slowly converted to the crystalline dihydroxypyrone (V).

The Diacetate (VI)

Into a small flask we introduced 6 g of the crystalline dihydroxypyrone (V) and 35 g of freshly-distilled acetic anhydride, added two drops of concentrated sulfuric acid, and the solution was allowed to stand at room temperature for a day. On addition of sulfuric acid the mixture warmed up considerably and acquired a dark color. After a day, the reaction mass was boiled under reflux for 8 hours. The cooled reaction product was poured in a thin stream into 75 ml of ice water, the acetic acid was neutralized with soda, the diacetate was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. As a result of two distillations we obtained 4 g of the diacetate (VI) as a colorless, almost odorless, syrupy liquid:

B.p. 128-130° (4 mm), n_D^{20} 1.4575, d_4^{20} 1.1760, MR 56.60; calculated 55.76.

Found %: C 53.94, 54.41; H 6.53, 6.50; $COCH_3$ 35.76. M 234, 236 (in benzene). $C_{11}H_{16}O_6$. Calculated %: C 54.10; H 6.56; $2COCH_3$ 35.25. M 244.

The diacetate (VI) was insoluble in water, but soluble in the usual organic solvents.

Acetylation of the Triol (VII)

3 drops of concentrated sulfuric acid were added to a solution of 8 g of the liquid triol (VII) in 57 g of freshly-distilled acetic anhydride. The solution warmed up strongly and acquired a cherry-red color. Then the solution was heated on a boiling water bath for 10 hours. The cooled solution was poured into 150 ml of ice water, the acetic acid was neutralized with soda, the product was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. We obtained 6.4 g of the above-described diacetate (VI) as a colorless syrup:

B.p. 123° (2 mm), n_D^{20} 1.4570, d_4^{20} 1.1763, MR 56.50; calculated 55.76.

Found %: C 54.10, 54.39; H 6.40, 6.81. M 232, 231 (in benzene). $C_{11}H_{16}O_6$. Calculated %: C 54.10, H 6.56. M 244.

Action of Methylaniline on the Keto Dioxide (IV)

4 g of methylaniline (b.p. 195-196° at 748 mm, $n_D^{16.5}$ 1.4725) was added slowly to 5.5 g of the keto dioxide (IV). The temperature of the reaction mixture at this time increased from 16 to 22°. Then the mixture was allowed to stand at room temperature for a day and a half, after which the much-thickened mixture was heated on the water bath at a temperature of 50-55° for 6 hours. We obtained a viscous, cherry-red syrup, from which by fractional distillation we separated 2.3 g of 2,5-dimethyl-2-methylphenylaminomethyl-4-hydroxytetrahydrofuran-3-one (VIII) as a viscous, light-yellow, almost odorless liquid:

B.p. 153-156° (2 mm), n_D^{20} 1.5378, d_4^{20} 1.1249, MR 69.21; calculated 68.38.

Found %: C 67.05, 67.12; H 7.83, 7.79; N 5.48, 5.46; OH 7.30. M 241, 243 (in benzene). $C_{14}H_{18}O_2(OH)N$. Calculated %: C 67.47; H 7.63; N 5.62; OH 6.83. M 249.

2,5-Dimethyl-2-methylphenylaminomethyl-4-hydroxytetrahydrofuran-3-one (VIII) rapidly darkened on standing in the air, and did not form picrates.

Action of Benzylmercaptan on the Keto Dioxide (IV)

7.1 g of the keto dioxide (IV) and 6.2 g of benzylmercaptan (b.p. 63-64° at 4 mm, n_D^{18} 1.5758) were heated on an oil bath at 125-130° for 6 hours. A viscous, dark-red product formed, from which after vacuum distillation we obtained 7.6 g of 2,5-dimethyl-2-benzylmercaptomethyl-4-hydroxytetrahydrofuran-3-one (IX) as a viscous, red, oily liquid with a disagreeable odor, and with a b.p. of 144-146° (2 mm).

Found %: C 63.62, 63.20; H 6.70, 6.89; S 12.42, 11.72; OH 6.56, 6.89. $C_{14}H_{17}O_2(OH)S$. Calculated %: C 63.40; H 6.77; S 12.03; OH 6.39.

The sulfide (IX) was insoluble in water, but was soluble in alcohol, ether and other organic solvents. It slowly crystallized on standing.

The Keto Oxide (XI)

Into a solution of 144 g of the methoxy ketone (X) (b.p. 45-45.5° at 3 mm, n_D^{19} 1.4420) in 1 liter of methanol, cooled by means of ice and salt to −10°, we added simultaneously during 1 hour, with energetic mixing, 215 ml of a 18% solution of hydrogen peroxide and 45 ml of a 4 N aqueous solution of sodium hydroxide. The oxidation reaction took place very energetically and was accompanied by a strong evolution of heat from the reaction mixture. The oxidation was carried out at a temperature no higher than 0°, which was achieved by cooling the flask with a cooling mixture and by slow addition of the oxidizing agent. 40 minutes after introduction of the oxidizing agent into the reaction mixture, about 4 g of hydrogen peroxide (determined by titration of the sample with hyposulfite) remained, which corresponded to the excess which was introduced. In addition, the original slightly yellow color of the solution had completely faded. The sodium hydroxide was neutralized with 10% sulfuric acid, the sodium sulfate which came down was filtered off, and the methanol and a portion of the water were removed in vacuo. Salt was added to the residue; the reaction product was extracted three times with ether, dried with sodium sulfate and after removal of the ether was vacuum distilled.

We obtained 108 g of the keto oxide (XI) as a colorless liquid with a mild, specific odor.

B.p. 57-57.5° (2 mm), n_D^{20} 1.4368, d_4^{20} 0.9986, MR 41.21; calculated 40.94.

Found %: C 60.60, 60.43; H 9.05, 8.70. M 157, 156 (in benzene). $C_8H_{12}O_3$. Calculated %: C 60.76; H 8.86. M 158.

The 2,4-dinitrophenylhydrazone consisted of fine, orange-colored crystals with a m.p. of 146-148° (from alcohol, precipitated only after evaporation of a large portion of the latter).

Found %: N 16.71, 16.75. $C_{14}H_{16}O_6N_4$. Calculated %: N 16.57.

The keto oxide (XI) was soluble in water and in the usual organic solvents. It polymerized appreciably on long storage.

Hydrolysis of the Keto Oxide (XI)

A solution of 34 g of the keto oxide (XI) in 450 ml of distilled water was refluxed for 4 hours at a temperature of 70-75°, and then was boiled under reflux for 12 hours. 6 hours after the heating began, drops of an oily product began to appear at the bottom of the flask, the quantity of which had hardly increased at the end of the hydrolysis. The light-yellow solution was evaporated in vacuo at a bath temperature of 32-35° to a viscous syrup (yellow color). The aqueous distillate was saturated with potash and extracted three times with ether, and the syrup was added to the combined ether extracts. The ether solution was dried with sodium sulfate, and after removal of the ether the product was vacuum distilled. We obtained 3 g of the original keto oxide (XI), and 19.5 g of the keto glycol (XII) as a viscous, odorless liquid.

B.p. 100-101° (2 mm), n_D^{20} 1.4608, d_4^{20} 1.1008, MR 43.88; calculated 43.85.

Found %: C 54.45, 54.63; H 9.09, 9.02; OH 20.13, 19.87; CH_3O 17.07 (according to Zeisel). M 173, 175 (in benzene). $C_8H_{16}O_5$. Calculated %: C 54.55; H 9.09; 2OH 19.31; $1CH_3O$ 17.61. M 176.

The keto glycol (XII) was highly soluble in water and alcohol, but less soluble in ether and benzene. It did not form crystalline carbonyl group derivatives.

The Diacetate (XIII)

To a solution of 12 g of the keto glycol (XII) in 25 g of freshly-distilled acetic anhydride, 2-3 drops of concentrated sulfuric acid were added, and at the same time the mixture warmed up appreciably and acquired a reddish color. We connected the reaction flask to a reflux condenser and heated it on a boiling water bath for 10 hours. The mixture was cooled, and then poured into 250 ml of ice water, the acetic acid was neutralized with soda, the diacetate was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. We obtained 8.5 g of the diacetate (XIII) as a colorless, odorless, viscous liquid.

B.p. 116° (2.5 mm), n_D^{20} 1.4512, d_4^{20} 1.1066, MR 63.17; calculated 62.58.

Found %: C 55.78, 55.77; H 7.46, 7.40. M 258, 261 (in benzene). $C_{12}H_{20}O_6$. Calculated %: C 55.38; H 7.69. M 260.

The diacetate (XIII) was soluble in the usual organic solvents, but was insoluble in water.

Action of Aniline on the Keto Oxide (XI)

12 g of the keto oxide (XI) and 7 g of freshly-distilled aniline were heated on the water bath at a temperature of 75-80° for 12 hours. A viscous, cherry-colored oil formed, and as a result of its vacuum distillation we obtained 8 g of phenylaminofuranone (XIV) as a viscous, yellow liquid with a specific odor.

B.p. 152-153° (3 mm), 144.5-146° (2 mm), 138-140° (1 mm), n_D^{20} 1.5575, d_4^{20} 1.1265, MR 62.52; calculated 61.87.

Found %: C 70.85, 71.47; H 7.40, 7.76; N 6.06, 6.87. M 219, 214 (in benzene) $C_{13}H_{17}O_2N$. Calculated %: C 71.23; H 7.76; N 6.85. M 219.

Found: number of active hydrogens, 0.99, 0.95 (according to Chugaev-Tserevitinov).

The semicarbazone consisted of colorless crystals with a m.p. of 203-205° (from aqueous alcohol).

Found %: N 20.69, 20.00. $C_{14}H_{20}O_2N_6$. Calculated %: N 20.29.

On passage of dry hydrogen chloride through a solution of phenylaminofuranone (XIV) in dry ether, the white, amorphous deposit of the hydrochloride precipitated, which was highly soluble in water, alcohol and chloroform, but deliquesced in air. On addition of an alcoholic solution of picric acid to an alcoholic solution of the phenylaminofuranone (XIV) a precipitate formed, which later came down as a dark oil, which was soluble in an excess of alcohol. We were unable to obtain the crystalline picrate.

Acetylation of Furanone (XIV)

9.3 g of phenylaminofuranone (XIV) was dissolved in 50 g of freshly-distilled acetic anhydride, and with or without addition, 3 drops of concentrated sulfuric acid, it was heated on the water bath for 8 hours. The reaction product was poured in a thin stream into 150 ml of ice water, the acetic acid was neutralized with soda, the acetate was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. We obtained 6 g of the amine as a viscous, odorless syrup.

B.p. 158-160° (1 mm), n_D^{20} 1.5420, d_4^{20} 1.1254, MR 72.98; calculated 71.48.

Found %: C 68.64, 68.54; H 7.54, 7.55; N 5.23, 5.51. M 257 (in benzene). $C_{12}H_{19}O_3N$. Calculated %: C 68.97; H 7.28; N 5.35, M 261.

The amine was insoluble in water, and was stable on storage. It partially crystallized on standing.

Action of Nitrous Acid on Furanone (XIV)

4 g of phenylaminofuranone (XIV) was dissolved in 50 ml of 12% hydrochloric acid, the mixture was cooled to 0°, and then 3 g of sodium nitrite in 5 ml of water was added slowly, with shaking, and it was allowed to stand in ice water for 30 minutes. The solution was neutralized with soda, and the green nitroso-compound which separated was extracted with ether. The ether extract was dried with sodium sulfate, filtered, and the major part of the ether was evaporated. The green-colored crystals of the nitroso-compound (nitrosamine) which precipitated were separated and recrystallized from a small amount of benzene. We obtained 1.6 g of the nitrosamine as characteristic green crystals with a m.p. of 120°.

Found %: N 11.79, 11.40. $C_{13}H_{17}O_3N_2$. Calculated %: N 11.29.

Action of Ethylamine on the Keto Oxide (XI)

A mixture consisting of 16 g of the keto oxide (XI) and 4.5 g of ethylamine (b.p. 16°) was heated in the presence of traces of water, in a sealed ampoule on the water bath for 2 hours at 55-60°, and for 4 hours at a temperature of 75-80°. We observed a warming up of the mixture (from 17 to 32°) on mixing the components, and observed the appearance of a light-yellow color. The color gradually deepened to a cherry-red color on heating the mixture.

The cooled ampoule was opened, and the reaction product was vacuum distilled. We obtained 11.5 g of 2,5-dimethyl-2-ethylaminomethyltetrahydrofuran-3-one (XV) as a light-yellow liquid with an amine odor.

B.p. 85-86° (5 mm), 78-79° (3 mm), n_D^{20} 1.4645, d_4^{20} 1.0043, MR 47.05; calculated 46.70.

Found %: C 63.00, 62.98; H 9.99, 10.10; N 8.02, 8.07. M 164, 173 (in benzene). $C_9H_{17}O_2N$. Calculated %: C 63.16; H 9.94; N 8.19. M 171.

The picrate consisted of fine, dark-yellow, acicular crystals which were readily soluble in alcohol, and were precipitated from the latter only by removal of a large portion of the solvent, and its m.p. was 207° (with partial decomposition).

Found %: N 14.33, 14.29. $C_{12}H_{28}O_3N_4$. Calculated %: N 14.00.

Found: number of active hydrogens, 1.01, 0.99 (according to Chugaev-Tserevitinov).

The ethylaminofuranone (XIV) was soluble in water and alcohol, and less soluble in ether and benzene. It darkened rapidly on standing in the air.

Acetylation of Furanone (XV)

8 g of the aminofuranone (XV) and 52 g of freshly-distilled acetic anhydride were heated on a boiling water bath for 8 hours. The reaction mixture was poured in a thin stream into 130 ml of ice water; the acetic acid was neutralized with soda, the amide was extracted with ether, the ether extract was dried with anhydrous sodium sulfate, and after removal of the ether the residue was vacuum distilled. We obtained 1.8 g of the amide, which consisted of a viscous, light-yellow, odorless liquid:

B.p. 137-139° (2 mm), n_D^{20} 1.4735, d_4^{20} 1.0402, MR 57.48; calculated 56.59.

Found %: C 61.49; H 9.20; N 6.52. $C_{11}H_{19}O_3N$. Calculated %: C 61.97; H 8.92; N 6.57.

The Amide was insoluble in water, but soluble in organic solvents, and was stable on storage.

Action of Methylamine on the Keto Oxide (XI)

Into a 200-ml flask we introduced 16 g of the keto oxide (XI) and 90 ml of a 16.5% solution of methylamine in 99% methanol. On mixing the components, the temperature of the mixture rose from 14 to 22°, moreover, the mixture acquired a light-yellow color. The flask was closed with a stopper and allowed to stand at room temperature for 2 days. Then the contents were transferred to an ampoule and heated in the sealed ampoule on the water bath for 4.5 hours at a temperature of 70-75°. At the same time the reaction mixture acquired a cherry-red color (with a slight fluorescence), and its viscosity increased appreciably. The cooled ampoule was opened, and the excess of methylamine and methanol were removed at low vacuum. The residue was distilled at a lower pressure. As a result of repeated fractional distillation in vacuo we obtained 5.4 g of 2,5-dimethyl-2-methylaminomethyltetrahydrofuran-3-one (XVI) as a light-yellow liquid which had an amine odor:

B.p. 83-85° (6 mm), n_D^{20} 1.4773, d_4^{20} 1.0108, MR 43.85; calculated 42.20.

Found %: C 61.82, 61.79; H 9.96, 10.04; N 9.90, 9.98. M 170, 163 (in benzene); number of active hydrogens, 1.0, 0.98 (according to Chugaev-Tserevitinov). $C_8H_{15}O_2N$. Calculated %: C 61.15; H 9.56; N 8.92. M 157.

The furanone (XVI) probably contained a difficult-to-isolate admixture of the 3-methylimino derivative, which accounted for the elevated results of the elementary analysis for nitrogen.

On addition of a saturated alcoholic solution of picric acid to an alcoholic solution of the aminofuranone (XVI), a dark-colored oil separated out, but no crystalline picrate formed.

The aminofuranone (XVI) was soluble in water, alcohol and chloroform, but less soluble in ether. On standing in the air it darkened, being gradually converted to a dark-colored, viscous, resinous mass.

Action of Diethylamine on the Keto Oxide (XI)

15.8 g of the keto oxide (XI) and 7.3 g of diethylamine (b.p. 55°) were heated in a sealed ampoule on the water bath at a temperature of 75-80° for 4.5 hours, and the contents of the ampoule acquired a dark color. The cooled ampoule was opened, and the reaction product was vacuum distilled. We obtained 12.8 g of a rather viscous, light-yellow liquid, which corresponded in composition to furanone (XVII):

B.p. 88-90° (3 mm), n_D^{20} 1.4533, d_4^{20} 0.9586, MR 56.20; calculated 56.39.

Found %: C 65.87, 66.00; H 10.41, 10.74; N 7.12, 6.81. M 200, 204, (in benzene). $C_{11}H_{21}O_2N$. Calculated %: C 66.33; H 10.55; N 7.03. M 199.

Determination of parachor at 20° (according to Sugden): P found, 478.4, calculated, 471.3.

The product was poorly soluble in water, and on addition of an alcoholic solution of picric acid a dark oil separated out, but no crystalline picrate formed.

Action of Methylaniline on the Keto Oxide (XI)

5 g of the keto oxide (XI) and 3.6 g of methylaniline were heated in a sealed ampoule on the water bath at 75-80° for 14 hours. A viscous, red-colored product formed. The ampoule was opened, and the reaction product

was vacuum distilled. We obtained 5 g of furanone (XVIII) as a light-yellow, viscous liquid:

B.p. 148-150° (2.5 mm), n_D^{20} 1.5485, d_4^{20} 1.0752, MR 68.89; calculated 66.85.

Found %: C 71.95, 72.10; H 8.49, 8.36; N 6.10, 6.17. M 231, 229 (in benzene). $C_{14}H_{19}O_2N$. Calculated %: C 72.10; H 8.15; N 6.01. M 233.

The furanone (XVIII) was insoluble in water, and darkened on prolonged standing, but no crystalline picrate formed.

Action of Benzylmercaptan on the Keto Oxide (XI)

10 g of the keto oxide (XI) and 8 g of benzylmercaptan (b.p. 63-64° at 4 mm, n_D^{18} 1.5758) were heated on an oil bath for 15 hours at a temperature of 140-145°. The disagreeable odor of benzylmercaptan almost disappeared; the reaction mixture became a dark-red color and thickened considerably. As a result of the vacuum distillation of the reaction product, we obtained 8 g of the keto furan sulfide (XIX) with a b.p. of 157-158° (2 mm), which consisted of a light-yellow, viscous liquid with a specific odor, and which crystallized on prolonged standing to colorless, plate-like crystals with a m.p. of 73° (after washing with cold methanol).

Found %: C 67.23, 67.34 H 7.05, 7.07; S 12.72, 12.65. M 246, 248 (in benzene). $C_{14}H_{18}O_2S$. Calculated %: C 67.15; H 7.25; S 12.80. M 250.

The use of activated carbon, which usually catalyzes similar reactions [14], introduced no substantial change, but the product in this case crystallized more rapidly.

Action of Sodium-Malonic Ester on the Keto Oxide (XI)

To an alcoholic solution of sodium ethylate, prepared from 1.3 g of sodium and 20 ml of anhydrous alcohol, 7.5 g of freshly-distilled malonic ester was added, and to the suspension obtained 7 g of the keto oxide (XI) was added in small portions. Then the reaction flask and a reflux condenser with a closed calcium chloride tube was heated on the water bath for 14 hours with slight boiling of the alcohol. The alcohol was removed in vacuo, the residue was decomposed with 5% sulfuric acid, extracted with ether, dried with sodium sulfate, and after removal of the ether it was vacuum distilled. We obtained 3.5 g of condensation products with a b.p. of 137-170° (3 mm), from which as a result of subsequent distillation we separated 0.7 g of the lactone (XX) as a light-yellow, viscous oil with a b.p. of 160-163° (3 mm).

Found %: C 57.30, 57.00; H 7.65, 7.69. $C_{13}H_{20}O_5$. Calculated %: C 57.35; H 7.35.

The lactone (XX) partially crystallized on standing.

Action of Sodium-Acetoacetic Ester on the Keto Oxide (XI)

To an alcoholic solution of sodium ethylate, prepared from 1.5 g of sodium and 22 ml of anhydrous alcohol, 7 g of freshly-distilled acetoacetic ester (b.p. 69° at 10 mm, n_D^{18} 1.4205) was added. Then 8 g of the keto oxide (XI) was added in small portions. The reaction began at once, and the reaction mixture warmed up from 17 to 72°, and acquired a red color. The reaction flask was closed by a reflux condenser with a calcium chloride tube, and heated on the water bath at a slight boil of the alcohol for 12 hours. The alcohol was removed in vacuo, the residue was decomposed with 5% sulfuric acid, extracted with ether, dried with sodium sulfate and vacuum distilled. 2 g of a mixture of the initial substances was distilled, and we obtained 5 g of condensation products with a b.p. of 130-175° (3 mm), from which as a result of two subsequent distillations, we separated 1 g of the lactone (XXI) as a light-yellow oil with a b.p. of 153-157° (3 mm), which partially crystallized on standing.

Found %: C 59.35, 59.28; H 7.63, 7.65. $C_{12}H_{18}O_5$. Calculated %: C 59.50; H 7.44.

Formation of the Polymer XXII)

7 g of the keto oxide (XI), stored for about a year, was poured into distilled water, and white flocs of solid polymer precipitated. After three reprecipitations by water from methanol solution, we obtained about 2 g of the polymer (XXII) as an amorphous, white powder with a m.p. of 111-116°.

Found %: C 61.87; H 9.31; CH_3O 18.06 (according to Zeisel); OH 8.50, M 2210, 2274 (in benzene). $(C_9H_{14}O_3)_{14}$. Calculated %: C 60.76; H 8.86; CH_3O 19.62, 13OH 9.99. M 2212.

The Keto Oxide (XXIV)

Into a three-necked flask, equipped with a mechanical stirrer, thermometer and two dropping funnels, we introduced 60 g of the methoxy ketone (XXIII) (b.p. 81-83° at 11 mm, n_D^{20} 1.4505) diluted with 400 ml of methanol.

The solution was cooled to −10° by means of a mixture of ice and salt, and then with continuous energetic stirring, 88 ml of 18% hydrogen peroxide and 17 ml of a 4 N aqueous solution of sodium hydroxide were added simultaneously during 1.5 hours. The oxidation reaction took place very energetically and was accompanied by an evolution of heat. The cooling and the rate of addition of the oxidizing agent were regulated in such a way that the temperature of the solution did not exceed 0°. For completion of the oxidation reaction, after introduction of the oxidizing agent to the reaction flask, the flask was removed from the cooling bath, and with continuous stirring was kept at room temperature for 45-50 minutes, care being taken that the temperature of the reaction mixture did not exceed 20-25°. 1 hour and 20 minutes after the introduction of the oxidizing agent into the reaction mixture, 1.5 g of free hydrogen peroxide remained, which corresponded to the excess introduced. The solution was neutralized with 10% sulfuric acid, the sodium sulfate which deposited was filtered off, and the methanol was removed in vacuo; the reaction product was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. We obtained 50.5 g of the keto oxide (XXIV), which consisted of a colorless liquid with a mild, specific odor.

B.p. 75° (2 mm), n_D^{20} 1.4378, d_4^{20} 1.0110, MR 41.07; calculated 40.94.

Found %: C 60.45, 60.48; H 9.11, 8.86. M 156, 156 (in benzene). $C_8H_{14}O_3$. Calculated %: C 60.76; H 8.86. M 158.

The 2,4-dinitrophenylhydrazone consisted of orange-colored, acicular crystals with a m.p. of 120-122° (after washing with alcohol on the filter).

Found %: N 17.00, 17.32. $C_{14}H_{18}O_6N_4$. Calculated %: N 16.57.

The keto oxide (XXIV) was soluble in water and in the usual organic solvents.

Together with the keto oxide (XXIV) in the experiment described, we obtained 2.8 g of the α-diketone (XXV), which was a yellowish-green liquid with a characteristic odor, suggestive of the odor of biacetyl.

B.p. 87-89° (4 mm), n_D^{20} 1.4438, d_4^{20} 1.0505, MR 40.37; calculated 40.81.

Found %: C 60.25, 60.20; H 8.30, 8.46. $C_8H_{14}O_3$. Calculated %: C 60.76; H 8.86.

The bis-2,4-dinitrophenylhydrazone consisted of fine, orange crystals with a m.p. of 219° (from a mixture of alcohol and ethyl acetate).

Found %: N 21.75, 21.77. $C_{20}H_{22}O_8N_8$. Calculated %: N 21.64.

Hydrolysis of the Keto Oxide (XXIV)

37 g of the keto oxide (XXIV) was dissolved in 450 ml of distilled water and heated on a boiling water bath for 20 hours. On heating, the solution gradually acquired a light-yellow color. 7-8 hours after heating began, dark-colored oily drops appeared at the bottom of the flask, the quantity of which had not increased at the end of the hydrolysis. The solution was evaporated in vacuo to $\frac{1}{3}$ of its original volume, saturated with potash, repeatedly extracted with ether, dried with sodium sulfate and after removal of the ether was vacuum distilled. We obtained 16 g of the unaltered keto oxide (XXIV), and 10 g of the keto glycol (XXVI) as a viscous, colorless, odorless liquid.

B.p. 103° (2 mm), n_D^{20} 1.4632, d_4^{20} 1.0937. MR 44.34; calculated 43.85.

Found %: C 54.02, 54.31; H 8.83, 8.89; CH_3O 17.28 (according to Zeisel); OH 19.07, 19.06. M 174, 174 (in benzene). $C_8H_{16}O_4$. Calculated %: C 54.55; H 9.09; CH_3O 17.61; 2OH 19.31. M 176.

By heating 7 g of the keto oxide (XXIV) dissolved in 100 ml of 2% sulfuric acid on a boiling water bath for 20 hours, we obtained 2.5 g of the keto glycol (XXVI) and 2.5 g of the original keto oxide (XXIV). The hydrolysis of the keto oxide (XXIV) took place much more difficultly than did the hydrolysis of its isomer, the keto oxide (XI). The keto glycol (XXVI) was soluble in water and alcohol, but difficultly soluble in ether. It did not form crystalline carbonyl group derivatives.

The Diacetate (XXVII)

To a solution of 5 g of the keto glycol (XXVI) in 40 g of freshly-distilled acetic anhydride we added two drops of concentrated sulfuric acid, and the solution was boiled under reflux for 10 hours. The reaction product was poured in a thin stream into 100 ml of ice water, the acetic acid was neutralized with soda, the diacetate was extracted with ether, dried with sodium sulfate and vacuum distilled. We obtained 5 g of the diacetate (XXVII) as an odorless, light-yellow, viscous liquid.

B.p. 100-102° (2 mm), n_D^{20} 1.4508, d_4^{20} 1.1058, MR 63.24; calculated 62.58.

Found %: C 55.49, 55.49; H 7.54, 8.02. M 243, 242 (in benzene). $C_{12}H_{18}O_4$. Calculated %: C 55.38; H 7.69. M 230.

Action of Ethylamine on the Keto Oxide (XXIV)

16 g of the keto oxide (XXIV) and 4.5 g of ethylamine (b.p. 16.6°) were heated, in the presence of traces of moisture in a sealed ampoule, on the water bath for 2 hours at a temperature of 55-60°, and for 4 hours at a temperature of 75-80°. On mixing the components, the temperature of the mixture rose from 18 to 26°, and a light-yellow color appeared. On heating the reaction mixture, its viscosity increased and the light-yellow color changed to a dark-red color. The cooled ampoule was opened, and the reaction product was vacuum distilled. We obtained 8 g of 2-(α-ethylamino)-ethyl-4-methyltetrahydrofuran-3-one (XXVIII) as a light-yellow liquid with a specific odor:

B.p. 84-86° (4 mm), n_D^{20} 1.4652, d_4^{20} 0.9951, MR 46.55; calculated 46.82.

Found %: C 63.63, 63.15; H 10.47, 9.95; N 8.28, 8.24. M 173, 173 (in benzene). $C_9H_{17}O_2N$. Calculated %: C 63.16; H 9.94; N 8.19. M 171.

Found: number of active hydrogens, 1.01, 0.97 (according to Chugaev-Tserevitinov).

The aminofuranone (XXVIII) was soluble in water, alcohol and chloroform, but less soluble in ether and benzene; it darkened on standing. On addition of an alcoholic solution of picric acid to the aminofuranone (XXVIII) a dark-colored oil, which was soluble in an excess of alcohol, separated.

Action of Aniline on the Keto Oxide (XXIV)

A solution of 15.5 g of the keto oxide (XXIV) in 9 g of freshly-distilled aniline was heated, in the presence of traces of water, on an oil bath for 19 hours at a temperature of 105-110°. On mixing the components, the temperature of the solution increased by 6° and the solution acquired a yellow color. After heating, a viscous, dark-cherry colored, oily product was obtained, by vacuum distillation of which we separated 6.5 g of 2-α-(phenylamino)-ethyl-4-methyltetrahydro-3-furanone (XXIX), a light-yellow, viscous oil which darkened rapidly on storage.

B.p. 142-144° (2 mm), n_D^{20} 1.5620, d_4^{20} 1.1233, MR 63.22; calculated 62.09.

Found %: C 70.81, 71.92; H 7.63, 7.56; N 6.89, 6.81. M 213, 220 (in benzene). $C_{14}H_{17}O_2N$. Calculated %: C 71.23; H 7.76; N 6.39. M 219.

Found: number of active hydrogens, 1.0, 1.06 (according to Chugaev-Tserevitinov).

The 2-phenylaminoethylfuran-3-one (XXIX) was difficultly soluble in water, but soluble in the usual organic solvents, and in storage it resinified. By the action of an alcoholic solution of picric acid oniit, a dark oil which was soluble in an excess of alcohol separated.

Action of Diethylamine on the Keto Oxide (XXIV)

7 g of the keto oxide (XXIV), 3.2 g of diethylamine (b.p. 55°) and 3 ml of alcohol were mixed, and the mixture was heated in a sealed ampoule on the water bath for 2 hours at 50-55°, and for 9 hours at 70-75°. The reaction mixture acquired a dark-cherry color and became more viscous. The cooled ampoule was opened, the alcohol and the residue of diethylamine were removed at low vacuum, then the vacuum was increased and the reaction product was distilled. We obtained 3.5 g of furanone (XXX) as a light-yellow liquid with an amine odor:

B.p. 92-95° (2 mm), n_D^{20} 1.4515, d_4^{20} 0.9612, MR 55.79; calculated 56.39.

Found %: C 66.02, 65.02; H 10.60, 10.51; N 6.98, 6.82. M 195, 192 (in benzene). $C_{11}H_{21}O_2N$. Calculated %: C 66.33; H 10.55; N 7.03. M 199.

Action of Benzylmercaptan on the Keto Oxide (XXIV)

9.7 g of the keto oxide (XXIV) and 8 g of benzylmercaptan (b.p. 63-64° at 4 mm, n_D^{18} 1.5758) were heated in a small flask with a vent tube on an oil bath for 27 hours at 140-145°. The viscous, red product which formed was vacuum distilled. As a result of vacuum fractional distillation of the reaction product, we obtained 10.3 g of 4-methyl-2-(α-benzylmercapto)-ethyltetrahydrofuran-3-one (XXXI) as a viscous, light-yellow liquid with a disagreeable, specific odor:

B.p. 136-138° (2 mm), n_D^{20} 1.4540, d_4^{20} 1.1018, MR 71.61; calculated 70.90.

Found %: C 67.16, 66.82; H 7.56, 7.46; S 12.67, 12.59. M 245, 249 (in benzene). $C_{14}H_{18}O_2S$. Calculated %: C 67.15; H 7.25; S 12.80. M 250.

Moreover, in this experiment 2.4 g of a product with a b.p. of 159-162° (3.5 mm) was separated, which crystallized as colorless, plate-like crystals with a m.p. of 71-72° (after washing with cold methanol) and which in all probability corresponded to 2,5-dimethyl-3-benzylmercaptotetrahydro-4-pyrone (XXXII).

Found %: C 66.72, 66.67; H 7.36, 7.12; S 13.49, 13.16. M 246 (in benzene). $C_{14}H_{18}O_2S$. Calculated %: C 67.15; H 7.25; S 12.80. M 250.

SUMMARY

By the action of alkaline hydrogen peroxide on 2-methyl-1,4-hexadien-3-one (III), 5-methoxy-2-methyl-1-hexen-3-one (X) and 1-methoxy-2-methyl-4-hexen-3-one (XXIII), a keto dioxide (IV) and the keto oxides (XI) and (XXIV) were obtained in a yield of 64-76%.

The keto oxides obtained were converted to the corresponding heterocyclic ketones of the pyran or furan series by the action of water, amines and mercaptans.

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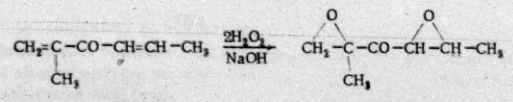
* See Consultants Bureau Translation, page 683.

ACETYLENE DERIVATIVES. 168.

α-KETO OXIDES AND THEIR TRANSFORMATIONS. V. THE OXIDES OF 1,4-HEXADIEN-3-ONE, 5-METHYL-2,5-HEPTADIEN-4-ONE AND 2-METHOXY-5-METHYL-5-HEPTEN-4-ONE

I. N. Nazarov, A. A. Akhrem and I. G. Tishchenko

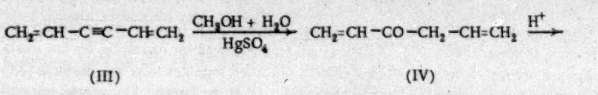
In the preceding report it was shown [1] that propenyl isopropenyl ketone (I), by the action of alkaline hydrogen peroxide, forms a 64% yield of the keto dioxide (II):



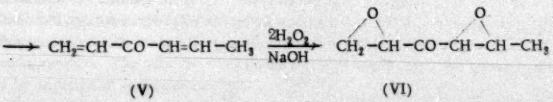
(I) (II)

In connection with the availability of the vinyl propenyl ketones, thanks to the convenient method developed in our laboratory for their production [2], it was of interest to study the action of alkaline hydrogen peroxide on other compounds of this series.

Vinyl propenyl ketone (V), easily obtainable by hydration of divinylacetylene (III) in an aqueous solution of methanol, in the presence of mercuric sulfate, was energetically oxidized by alkaline hydrogen peroxide in a dioxan solution, with cooling, forming a 62% yield of the keto dioxide (VI):

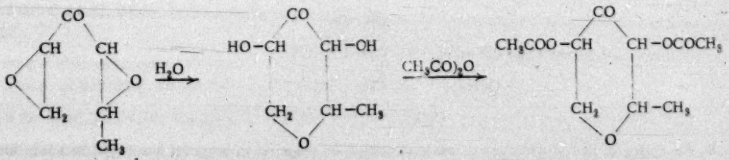


(III) (IV)



(V) (VI)

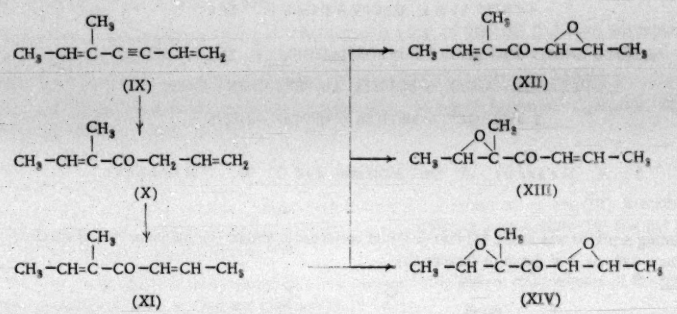
Hydrolysis of the keto dioxide (VI) scarcely proceeded at room temperature, which is explained by the absence of a tertiary carbon atom, even if only in one of the two oxide rings. Hydrolytic cleavage of the oxide rings proceeds on prolonged heating of the keto dioxide (VI) with water, with the formation of 2-methyl-3,5-dihydroxytetrahydro-4-pyrone (VII)



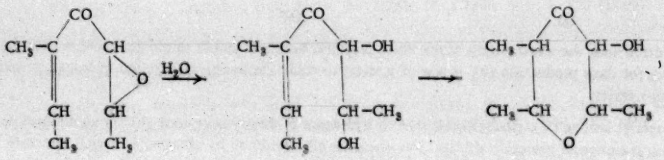
(VI) (VII) (VIII)

On hydrolysis of the keto dioxide (VI), the crystalline dihydroxypyrone (VII) (m.p. 158°), was produced in a small amount but the chief hydrolysis product was a viscous syrup, which was highly soluble in water and in alcohol, and which was probably a mixture of the isomers of dihydroxypyrone (VII). The diacetate (VIII) was obtained by the action of acetic anhydride on this syrup.

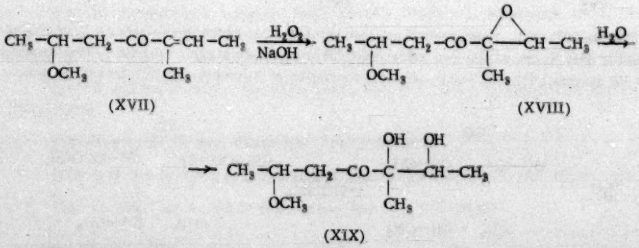
By oxidation, with alkaline hydrogen peroxide, of 5-methyl-2,5-heptadien-4-one (XI) (the high-boiling isomer), obtained by hydration of the dienyne (IX), a mixture of the keto oxides (XII), (XIII) and (XIV) formed in a total yield of about 60%.



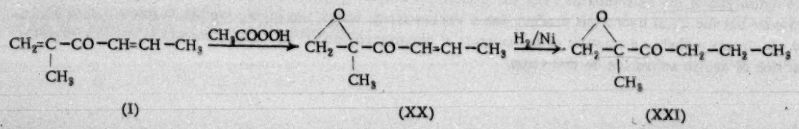
The monoxide (XII), which on long heating with water hydrolyzed to 2,5,6-trimethyl-3-hydroxytetrahydro-4-pyrone (XVI), was the chief oxidation product.



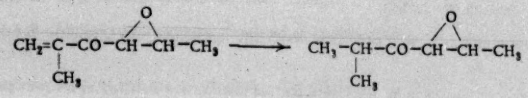
The larger yield of the keto oxide (XII) indicated the easier oxidizability, by alkaline hydrogen peroxide, of the less substituted double bond in the dienone (XI). This may also be observed, for example, by the oxidation which we carried out for 2-methoxy-5-methyl-5-hepten-4-one (XVII), obtained together with the dienone (XI) by the hydration of 5-methyl-1,5-heptadien-3-yne (IX) in an aqueous solution of methanol. For oxidation to the corresponding keto oxide (XVIII) (with a yield of 60%), the methoxy ketone (XVII) required more than a double excess of alkaline hydrogen peroxide, moreover, the oxidation reaction was carried out almost without cooling. The keto glycol (XIX) was formed by heating the keto oxide (XVIII) with water.



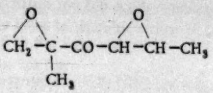
By the action of acetyl hydrogen peroxide (2 moles) on propenyl isopropenyl ketone (I) in a solution of dry ether, we obtained a 20% yield of the unsaturated monoxide (XX), which on hydrogenation over Raney nickel, formed the saturated keto oxide (XXI).



By the action of one molecule of alkaline hydrogen peroxide on propenyl isopropenyl ketone (I) in a solution of acetone, on cooling, we obtained about a 20% yield of the unsaturated monoxide, which in all probability, had the structure (XXII). Together with this, we obtained a small quantity of the earlier-described [1] keto dioxide (XXIV).



(XXII) (XXIII)



(XXIV)

The keto oxide (XXII), on hydrogenation over Raney nickel, added 2 atoms of hydrogen, and was converted to the saturated keto oxide (XXIII). As we showed earlier [3, 4], β,β-dimethyldivinyl ketone, by the action of one molecule of alkaline hydrogen peroxide, also formed the unsaturated monoxide, moreover, the oxygen added chiefly at the unsubstituted vinyl group.

EXPERIMENTAL

The Keto Dioxide (VI)

Into a 1-liter, three-necked flask, equipped with a mechanical stirrer, thermometer and two dropping funnels, we introduced 400 ml of dioxan and 46 g of vinyl propenyl ketone (V), which was obtained by the hydration of divinylacetylene in an aqueous solution of methanol in the presence of mercury sulfate [5] (b.p. 39-41° at 12 mm, n_D^{19} 1.4710). During 1 hour and 50 minutes, 195 ml of 18% solution of hydrogen peroxide and 12 ml of a 4 N aqueous solution of sodium hydroxide were added simultaneously, with stirring, to the solution chilled to −4°. The oxidation reaction was accompanied by a strong increase of temperature, the latter being kept at not above + 5° by means of a cooling mixture and by slow introduction of the oxidizing agent.

40 minutes after the introduction of the oxidizing agent into the solution, 3.6 g of hydrogen peroxide remained, which by calculation of the excess (4.5 g) which was introduced, indicated complete reaction of the hydrogen peroxide. In addition to this, the light-yellow color of the solution and the pungent odor native to vinyl propenyl ketone had completely disappeared. The solution was neutralized with 10% sulfuric acid, and the excess hydrogen peroxide was decomposed by addition of manganese dioxide to the reaction mixture; the sodium sulfate which came down was filtered off, the dioxan and a portion of the water were removed in vacuo, the product was extracted with ether, dried with sodium sulfate and after removal of the ether was vacuum distilled. 37.7 g of the keto dioxide (VI) was obtained as a colorless liquid with a mild, specific odor.

B.p. 74-76° (2 mm), n_D^{20} 1.4545, d_4^{20} 1.1405, MR 30.40; calculated 30.02.

Found %: C 54.87, 54.80; H 6.77, 6.56. M 130, 133 (in benzene). $C_6H_8O_3$. Calculated %: C 55.17; H 6.25. M 128.

We were unable to recrystallize the 2,4-dinitrophenylhydrazone, after washing the orange-colored, fine crystals, with a m.p. of 212-213°, on the filter with methanol.

Found %: N 18.67, 18.70. $C_{12}H_{12}O_6N_4$. Calculated %: N 18.18.

The keto dioxide (VI) was soluble in water and in the usual organic solvents.

Hydrolysis of the Keto Dioxide (VI)

On standing of a solution of 7.5 g of the keto dioxide in 40 ml of distilled water for 12 days at room temperature, almost all of the keto dioxide was recovered without appreciable formation of hydrolysis products. In connection with this, a solution of 16 g of the keto dioxide (VI) in 150 ml of distilled water was heated on the water bath at 85-90° for 30 hours. The light-yellow solution was filtered and evaporated in vacuo at a bath temperature of 32-34°. 20 g of a yellow, water-soluble, viscous syrup was obtained. On prolonged standing of the syrup in a vacuum-

desiccator over phosphoric anhydride, a small quantity of a solid product formed in it. The syrup was diluted with dry chloroform and the crystals were separated by filtration at low vacuum, washed with chloroform and recrystallized from alcohol. 0.65 g of the dihydroxypyrone (VII) was obtained as fine, colorless crystals with a m.p. of 158°.

Found %: C 49.48, 49.54; H 7.11, 6.68; OH 23.56, 23.39. M 149, 149 (according to Rast). $C_6H_{10}O_4$. Calculated %: C 49.32; H 6.85; 2OH 23.29. M 146.

The dihydroxypyrone (VII) was rather difficultly soluble in water and in alcohol, and insoluble in ether, benzene and chloroform.

After removal of the chloroform at low vacuum, the liquid portion (syrup) was distilled at a lower pressure. 11.5 g of a light-yellow, almost odorless, viscous syrup, with a b.p. of 101-109° (3 mm), was distilled. In the flask was a residue (about 7 g) of a very viscous, yellow product which did not distill in vacuo (3 mm) at a bath temperature of 190°. An attempt to crystallize it by cooling it with a solution of solid carbon dioxide in acetone did not yield positive results.

In the distilled syrup, crystals of the dihydroxypyrone (VII) (0.7 g) soon precipitated, which after recrystallization melted at 158° and gave no m.p. depression with the form described above

The residue was vacuum distilled again. We obtained about 8 g of an almost colorless, viscous syrup which was soluble in water, alcohol and pyridine, insoluble in ether and benzene, and was a mixture of the dihydroxypyrone (VII) isomers:

B.p. 103-105° (3 mm), n_D^{20} 1.4903, d_4^{20} 1.2776, MR 33.08; calculated 33.11.

Found %: C 49.55, 49.43; H 6.81, 7.25; OH 23.30, 23.52. M 144, 145 (in dioxan). $C_6H_{10}O_4$. Calculated %: C 49.32; H 6.85; 2OH 23.29. M 146.

The substance, with 2,4-dinitrophenylhydrazine and semicarbazide, did not form crystalline carbonyl group derivatives. On standing, it slowly crystallized to dihydroxypyrone (VII).

The Diacetate (VIII)

Two drops of concentrated sulfuric acid were added to a solution of 6 g of the dihydroxypyrone (VII) (b.p. 103-104° at 3 mm) in 40 g of freshly-distilled acetic anhydride; at this time the mixture darkened and its temperature increased from 18 to 53°. Then the mixture was boiled under reflux for 8 hours. The contents of the flask were cooled and poured into 75 ml of ice water. The acetic acid was neutralized with soda, the acetate was extracted with ether, dried with sodium sulfate and vacuum distilled. 2.2 g of the diacetate (VIII) was obtained as a colorless, odorless, viscous liquid:

B.p. 118-120° (2 mm), n_D^{20} 1.4660, d_4^{20} 1.1997, MR 52.06; calculated 51.14.

Found %: C 54.34, 54.31; H 5.84, 6.00; CH_3CO 36.96. $C_{10}H_{14}O_6$. Calculated %: C 54.17; H 6.10; $2CH_3CO$ 36.09.

The Keto Oxides (XII, XIII and XIV)

Into a 1-liter, three-necked flask, equipped with a mechanical stirrer, thermometer and two dropping funnels, we introduced 260 ml of dioxan and 42.5 g of the high-boiling isomer of 5-methyl-2,5-heptadien-4-one (XI) (b.p. 69-71° at 9 mm, n_D^{20} 1.4820), which was obtained by the hydration of 5-methyl-1,5-heptadien-3-yne [6]. To the solution cooled to −5°, we added simultaneously during 1 hour and 15 minutes, with energetic stirring, 150 ml of 18% solution of hydrogen peroxide and 17 ml of a 4 N aqueous solution of sodium hydroxide. The oxidation was accompanied by the evolution of heat. Cooling the flask with the cooling mixture, the rate of introduction of oxidizing agent was regulated so that the temperature of the reaction mixture did not exceed 2-3°. 20 minutes after introduction of the oxidizing agent into the reaction mixture, 14.5 g of hydrogen peroxide (determined by titration of a sample with 0.1 N solution of hyposulfite) remained from the total quantity of 27 g introduced (2 moles, 3.7 g excess). The flask was removed from the cooling bath, and kept for 2 hours at room temperature, with stirring. The hydrogen peroxide content decreased during this time to 11.2 g, and remained without further change. The alkali was neutralized with 10% sulfuric acid, the rest of the hydrogen peroxide was decomposed with manganese dioxide, the sodium sulfate was filtered off, and the dioxan and a portion of the water were removed in vacuo; the product was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. As a result of repeated fractional distillation, the following fractions were separated: 1st, b.p. 54-54.5° (2 mm), n_D^{20} 1.4762, 18 g; 2nd, b.p. 69-71° (2 mm), n_D^{20} 1.4690, 3.5 g; 3rd, b.p. 83-84° (2 mm), n_D^{20} 1.4545, 6.5 g.

The 1st fraction corresponded to the keto monoxide (XII) and was a colorless, mobile liquid with a characteristic odor:

B.p. 54-55.5° (2 mm), n_D^{20} 1.4762, d_4^{20} 0.9916, MR 40.02; calculated 39.96.

Found %: C 68.38, 68.17; H 8.84, 8.96. $C_9H_{12}O_2$. Calculated %: C 68.57; H 8.57.

The 2,4-dinitrophenylhydrazone consisted of friable, orange-colored, acicular crystals with a m.p. of 178-179° (from alcohol).

Found %: N 17.64, 17.81. $C_{15}H_{18}O_6N_4$. Calculated %: N 17.50.

The keto oxide (XII) was soluble in water and organic solvents, decolorized a solution of bromine in chloroform, thickened on storage in the air, and did not change on storage in a sealed ampoule.

The 2nd fraction corresponded to the keto monoxide (XIII) and was a colorless, mobile liquid of specific odor, which slowly thickened on storage in the air:

B.p. 69-71° (2 mm), n_D^{20} 1.4690, d_4^{20} 1.0091, MR 38.64; calculated 38.92.

Found %: C 68.82, 68.37; H 9.10, 8.99. $C_9H_{12}O_2$. Calculated %: C 68.57; H 8.57.

The 3rd fraction corresponded to the keto dioxide (XIV) and was a colorless, almost odorless liquid:

B.p. 83-84° (2 mm), n_D^{20} 1.4545, d_4^{20} 1.0768, MR 39.52; calculated 39.44.

Found %: C 61.77, 61.83; H 7.87, 7.83. M 152, 156 (in benzene). $C_9H_{12}O_3$. Calculated %: C 61.54; H 7.69. M 156.

We were unable to recrystallize the 2,4-dinitrophenylhydrazone; after washing it on the filter with methanol, it melted at 257° (decomposition).

Found %: N 17.28, 17.25. $C_{15}H_{18}O_7N_4$. Calculated %: N 16.67.

The keto oxide (XIV) was soluble in water and in organic solvents.

Hydrolysis of the Keto Oxide (XII)

A solution of 10 g of the keto oxide (XII) in 170 ml of distilled water was heated on a boiling water bath for 25 hours. After evaporation of the water in vacuo, a small quantity of a reddish-colored, viscous substance was obtained in the residue. The aqueous distillate was saturated with potash and extracted with ether. The residue in the flask and the ether extracts were combined, dried with sodium sulfate, and after removal of the ether the residue was distilled in vacuo. 5 g of the original oxide (XII) and 1.5 g of the unsaturated keto glycol (XV) were obtained as a light-yellow, viscous liquid:

B.p. 103° (2 mm), n_D^{20} 1.4815, d_4^{20} 1.0494, MR 42.88; calculated 41.89.

Found %: C 61.71, 61.35; H 9.23, 9.13; OH 20.54, 20.87. $C_9H_{14}O_3$. Calculated %: C 60.76; H 8.86; 2OH 21.52.

In the keto glycol (XV), on standing, crystals formed, probably crystals of the hydroxypyrone (XVI), which, because of their small quantity, were not studied closely.

The Keto Oxide (XVIII)

Into a 0.5-liter, three-necked flask, equipped with a mechanical stirrer, thermometer and two dropping funnels, we introduced 15.5 g of the methoxy ketone (XVII) (b.p. 81-83° at 10 mm, n_D^{20} 1.4565) [6], diluted with 100 ml of methanol. During 40 minutes, with energetic stirring, 25 ml of an 18% solution of hydrogen peroxide (4.5 g of peroxide, as compared to 3.4 g required theoretically) and 6 ml of a 4 N aqueous solution of sodium hydroxide were run into the solution cooled to −4°. 1 hour and 20 minutes after introduction of the oxidizing agent into the reaction mixture, there remained 3.57 g of hydrogen peroxide (found by titration of a sample with a 0.1 N solution of hyposulfite). The reaction mixture was left at room temperature for a night, and during this time the hydrogen peroxide content decreased to 2.68 g. Then to the reaction mixture, with stirring, 25 ml more of 18% solution of hydrogen peroxide and 5 ml of a 4 N aqueous solution of sodium hydroxide were added in small portions. On stirring of the reaction mixture for 1 hour and 40 minutes, the quantity of combined hydrogen peroxide amounted to 3.32 g, which practically proved the completion of the oxidation reaction. The solution was neutralized with 10% sulfuric acid, the excess hydrogen peroxide was decomposed with manganese dioxide, and the sodium sulfate was

filtered off; the solvent was removed in vacuo, the reaction product was extracted with ether, dried by sodium sulfate and after removal of the ether was vacuum distilled. 9.8 g of the keto oxide (XVIII) was obtained as a colorless liquid with a mild, specific odor:

B.p. 67-68° (2 mm), n_D^{20} 1.4575, d_4^{20} 1.0156, MR 46.15; calculated 45.56.

Found %: C 63.07, 62.71; H 9.41, 9.30. M 171, 174 (in benzene). $C_9H_{16}O_2$. Calculated %: C 62.79; H 9.30. M 172.

The 2,4-dinitrophenylhydrazone consisted of characteristic fine, orange-colored, acicular crystals with a m.p. of 169° (from alcohol).

Found %: N 15.90, 16.16. $C_{15}H_{22}O_8N_4$. Calculated %: N 15.91.

The keto oxide (XVIII) was soluble in water and in organic solvents.

Hydrolysis of the Keto Oxide (XVIII)

A solution of 6 g of the keto oxide (XVIII) in 60 ml of 2% sulfuric acid was heated on the water bath for 20 hours, during which the solution acquired a light-yellow color. The acid was neutralized with sodium bicarbonate, the solution was evaporated in vacuo to $\frac{1}{3}$ of its original volume, saturated with potash and repeatedly extracted with ether. The ether extracts were combined and dried with sodium sulfate, and after removal of the ether the product was vacuum distilled. 3.6 g of the keto glycol (XIX) was obtained as a rather viscous, odorless, almost colorless liquid:

B.p. 105-107° (2.5 mm), n_D^{18} 1.4600, d_4^{20} 1.0873, MR 47.86; calculated 48.47.

Found %: C 56.46, 56.61; H 9.14, 9.00; OH 18.12, 18.52. $C_9H_{18}O_4$. Calculated %: C 56.84; H 9.47; 2OH 17.90.

The keto glycol (XIX) was soluble in water and alcohol, but difficultly soluble in ether and benzene.

The Monoxide (XX)

We slowly added 52 g of a 90% acetic acid solution of acetyl hydrogen peroxide [8] (2 moles) to a solution of 32 g of propenyl isopropenyl ketone (I) (b.p. 60-61° at 26 mm, n_D^{18} 1.4700) in anhydrous ether [7] cooled to 0°. Then the mixture was allowed to stand at room temperature for 7 days. The solution was neutralized with a 10% solution of potassium hydroxide, the ether layer was washed with water, dried with sodium sulfate, and after removal of the ether the residue was vacuum distilled. We obtained 7.2 g of the unsaturated monoxide (XX), which was a colorless, very mobile liquid with a specific, pungent odor:

B.p. 49° (2 mm), n_D^{18} 1.4525, d_4^{20} 0.9929, MR 34.28; calculated 34.21.

Found %: C 66.44, 66.23; H 7.87, 8.22. M 127, 128 (in benzene). $C_7H_{10}O_2$. Calculated %: C 66.67; H 7.97. M 126.

From an ether solution of propenyl isopropenyl ketone and acetyl hydrogen peroxide (2 moles), on standing for about a month, the monoxide (XX) also formed, but its yield was lowered because of the formation of a large quantity of polymer.

The keto oxide (XX) was soluble in water, alcohol, ether and other organic solvents. It rapidly thickened to a viscous polymer on standing in the air, but on storage in a sealed ampoule no visible change was observed. The heating of an aqueous solution of the oxide led to the formation of a small yield of a viscous, water-soluble syrup (not investigated in detail).

Hydrogenation of the Keto Monoxide (XX)

3.2 g of the monoxide (XX) in 25 ml of ethanol was hydrogenated over Raney nickel. In 5 hours 540 ml of hydrogen had been absorbed, compared to 570 ml required theoretically for one double bond. The catalyst was filtered off, the ethanol was removed in vacuo at 130-135 mm, and the residue was distilled at a lower pressure. 1.7 g of the saturated keto oxide (XXI) was obtained as a colorless, hightly mobile liquid of a disagreeable ethereal odor:

B.p. 57-58° (9 mm), n_D^{20} 1.4275, d_4^{20} 0.9556. MR 34.41; calculated 34.68.

Found %: C 65.25, 65.35; H 9.31, 9.45. $C_7H_{12}O_2$. Calculated %: C 65.63; H 9.38.

The 2,4-dinitrophenylhydrazone consisted of characteristic bright orange-colored, friable needles with a m.p. of 203° (from alcohol).

Found %: N 18.57, 18.42. $C_{13}H_{16}O_8N_8$. Calculated %: N 18.18.

The Monoxide (XXII)

Into a 1.5-liter, three-necked flask, equipped with a thermometer, mechanical stirrer and two dropping funnels, we introduced 77 g of propenyl isopropenyl ketone (I), and 800 ml of dilute acetone. To the solution cooled to −8°, with energetic mixing, we added simultaneously during 45 minutes, 175 ml of a 15% solution of hydrogen peroxide and 12 ml of a 4 N aqueous solution of sodium hydroxide. Cooling the flask with a mixture of ice and salt, the oxidizing agent was introduced at such a rate that the temperature of the reaction mixture did not exceed 2-3° (above 0°). After 1 hour and 40 minutes, 3.5 g of hydrogen peroxide (26.25 g introduced) remained in the reaction mixture, which corresponded almost to the excess introduced, in comparison with the quantity required for one double bond (23.8 g). The sodium hydroxide was neutralized with 10% sulfuric acid, the rest of the hydrogen peroxide was decomposed by addition of manganese dioxide, the sodium sulfate was filtered off, and the acetone was removed in vacuo; the product was extracted with ether, dried with sodium sulfate, and after removal of the ether was vacuum distilled. As a result of repeated fractional distillation in vacuo, 16 g of the unsaturated monoxide (XXII) was obtained as a colorless, mobile liquid with a specific pungent odor:

B.p. 43° (3 mm), n_D^{18} 1.4482, d_4^{20} 0.9615, MR 34.86; calculated 34.21.

Found %: C 66.20, 66.56; H 8.28, 8.26. $C_7H_{10}O_2$. Calculated %: C 66.67; H 7.97.

The monoxide (XXII) was soluble in water and in the usual organic solvents. On standing in the air, it polymerized to a tough, viscous mass, solidifying to a brittle, clear polymer. 2 g of the earlier obtained keto dioxide (XIV) with a b.p. of 79° (1 mm), n_D^{20} 1.4510, separated, together with the keto oxide (XXII). The experiment took place with the formation of a large quantity of polymeric products.

Hydrogenation of the Monoxide (XXII)

5 g of the keto oxide (XXII) in 25 ml of ethanol was hydrogenated in the presence of Raney nickel. In 6 hours and 30 minutes 0.87 liter of hydrogen was absorbed, compared to the 0.89 liter required theoretically for one double bond. The first 0.65 liter was absorbed in 3 hours, then the rate of hydrogenation gradually decreased, and toward the end hydrogenation had practically ceased. The catalyst was filtered off, the alcohol was removed in vacuo (130 mm), and the residue was distilled at a lower pressure. 3.2 g of the saturated keto oxide (XXIII) was obtained as a colorless, highly mobile liquid, with a characteristic pleasant odor:

B.p. 62° (12 mm), n_D^{18} 1.4294, d_4^{20} 0.9494, MR 34.81; calculated 34.68.

Found %: C 65.30, 65.46; H 9.57, 9.23. $C_7H_{12}O_2$. Calculated %: C 65.63; H 9.38.

The 2,4-dinitrophenylhydrazone consisted of fine, acicular crystals with a m.p. of 129-130° (from alcohol).

Found %: N 18.02, 18.19. $C_{13}H_{16}O_8N_8$. Calculated %: N 18.18.

The keto oxide (XXIII) was stable on storage, and was soluble in water and in the usual organic solvents.

SUMMARY

By the action of alkaline hydrogen peroxide on vinyl propenyl ketones (I), (V) and (XI), and on the unsaturated methoxy ketone (XVII), which were obtained by hydration of the divinylacetylene hydrocarbons in an aqueous solution of methanol, a high yield of the corresponding α-keto dioxides (VI), (XIV) and α-keto oxides (XII), (XIII), (XVIII) and (XXII), was formed. The hydrolysis of the α-keto oxides was described.

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PRODUCTION OF BIS-PYRAN TYPE 3,4-DIKETONES OF THE FURANIDINE SERIES

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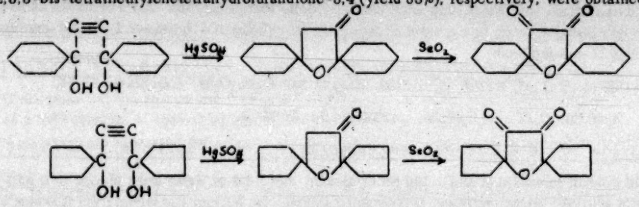
In a previous work it was shown that the oxidation by selenium dioxide of ketones of the tetrahydrofuran (furanidine) series, with tertiary carbon atoms in the 2,5-positions and a ketonic group in position 3, may serve as a convenient preparative method for the production of the corresponding α-diketones with carbonyl groups in the 3,4-positions [1].

In the present work the oxidation by selenium dioxide of other monoketones of the tetrahydrofuran series – 2,2,5,5-bis-pentamethylenetetrahydrofuranone-3 and 2,2,5,5-bis-tetramethylenetetrahydrofuranone-3 – was studied. These monoketones were obtained in high yields from the corresponding acetylene glycols, by simultaneous hydration and dehydration, with closing of the furanidine ring.

The reaction was carried out by long heating (10-15 hours) of aqueous suspensions of the glycols with a large quantity of mercury sulfate (30 g of mercury sulfate, instead of 10 g, per 50 g of the glycol), which made possible the production of high yields of the ketones – approximately 74% instead of 20% [2].

On oxidation of 2,2,5,5-bis-pentamethylenetetrahydrofuranone-3 and 2,2,5,5-bis-tetramethylenetetrahydrofuranone-3 by selenium dioxide in boiling dioxan, 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4 (yield 85%) and 2,2,5,5-bis-tetramethylenetetrahydrofurandione-3,4 (yield 83%), respectively, were obtained.



Both diketones consisted of bright crimson-colored crystals, which with water formed white hydrates.

Thus, we successfully used the oxidation by selenium dioxide for the production of bis-pyran type 3,4-diketones of the tetrahydrofuran series, for which the carbon atoms in the 2 and 5 positions of the furanidine ring entered simultaneously into the composition of the cyclohexane or cyclopentane ring.

EXPERIMENTAL

1. Preparation of 2,2,5,5-bis-Pentamethylenetetrahydrofuranone-3

50 g (0.23 mole) of bis-(1-hydroxycyclohexyl)-acetylene,* 15 g of mercury sulfate and 250 ml of water were placed in a liter, three-necked flask with a stirrer, reflux condenser, and dropping funnel; the mixture was boiled for 2 hours with energetic stirring, after which 15 g more of mercury sulfate was added, and the heating was continued for 8 hours longer. An oily liquid was separated from the water, and the water layer was extracted with ether. The ether extracts were combined with the oily layer, filtered off from the mercury, and hydrogen sulfide was passed through the solution until complete precipitation of the mercury sulfide. The latter was separated, and the solution was washed with soda and then with water, and dried with calcium chloride. After removal of the ether, the residue was vacuum distilled twice.

* Bis-(1-hydroxycyclohexyl)-acetylene was obtained by the Iotsich reaction by reaction of cyclohexanone with acetylenedimagnesium bromide; m.p. 107-108° [2, 3].

37 g (74%) of 2,2,5,5-bis-pentamethylenetetrahydrofuranone-3, which had the following constants, was obtained:

B.p. 141-142° (9 mm), n_D^{20} 1.4941, d_4^{20} 1.0336, MR_D 62.91. $C_{14}H_{22}O_3$. Calculated 61.90.

Semicarbazone b.p. 214-215°.

Literature data: b.p. 152-154° (18 mm), n_D^{20} 1.4904, d_4^{20} 1.0268 [2], semicarbazone b.p. 216° [2].

The thiosemicarbazone was obtained quantitatively from 1 g of the ketone in 5 ml of pyridine, and 1.5 g of thiosemicarbazide hydrochloride in 5 ml of water: its m.p. was 190-191° (from dilute alcohol).

Found %: N 14.34, 14.43. $C_{15}H_{25}ON_3S$. Calculated %: N 14.23.

The oxime. A solution of 1 g of hydroxylamine hydrochloride in 5 ml of water was added to a solution of 2.2 g of the ketone in 10 ml of pyridine. The mixture was refluxed for 2 hours, then it was poured into 100 ml of water. The precipitate was analyzed. The yield was quantitative. The m.p. was 125° (from anhydrous alcohol).

Found %: N 6.00, 5.78. $C_{14}H_{23}O_3N$. Calculated %: N. 5.92.

4-Benzylidene-2,2,5,5-bis-pentamethylenetetrahydrofuranone-3

15 drops of a 25% solution of sodium hydroxide was added to 2.2 g (0.01 mole) of the ketone and 1.06 g (0.01 mole) of benzaldehyde in 5 ml of alcohol. The precipitate which separated was recrystallized from alcohol. The yield was 1.7 g (55%); its m.p. was 100-101°.

Found %: C 81.03, 80.88; H 8.53, 8.45. $C_{21}H_{26}O_3$. Calculated %: C 81.27; H 8.42.

4-Bromo-2,2,5,5-bis-pentamethylenetetrahydrofuranone-3

A mixture of 15 g (0.067 mole) of 2,2,5,5-bis-pentamethylenetetrahydrofuranone-3 and 16.6 g (0.067 mole) of dioxan dibromide [4] was shaken in the cold for 4 hours. The reaction mass was diluted with ether, washed with water, soda, and then again with water, and dried with anhydrous sodium sulfate. After removal of the ether, the residue was vacuum distilled twice in a current of nitrogen. 19 g (94%) of 4-bromo-2,2,5,5-bis-pentamethylene-tetrahydrofuranone-3 was obtained:

B.p. 152-153° (4 mm), n_D^{20} 1.5250, d_4^{20} 1.2930, MR_D 71.34. $C_{14}H_{21}O_3Br$. Calculated 69.66.

Found %: Br 26.23, 26.38. $C_{14}H_{21}O_3Br$. Calculated %: Br 26.53.

II. Preparation of 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4

6 g (0.054 mole) of selenium dioxide, 100 ml of dioxan and 5 ml of water were placed in a half-liter, three-necked flask with a stirrer, reflux condenser and dropping funnel. On boiling and stirring the mixture energetically, 10 g (0.045 mole) of 2,2,5,5-bis-pentamethylenetetrahydrofuranone-3 was added dropwise during 15-20 minutes, after which the mixture was boiled for 12 hours. The color of the solution became dark-red, and selenium deposited on the walls of the flask. After cooling, the selenium was filtered off, washed with dioxan and dried. 2.8 g of selenium was extracted. The dioxan solutions were combined, the dioxan was removed, and the residue was dissolved in 200 ml of ether. The ether solution was filtered and dried with calcium chloride. After removal of the ether, the residue was vacuum distilled. We obtained 9.1 g (85%) of 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4, with a b.p. of 167-170° (16 mm), which crystallized in the vessel. After recrystallization from petroleum ether it melted at 69-70°. It was not described in the literature.

Found %: C 71.36, 71.20; H 8.65, 8.63. $C_{14}H_{20}O_3$. Calculated %: C 71.16; H 8.53.

The substance consisted of bright crimson-colored crystals, which were insoluble in water, but soluble in alcohol, ether and dioxan. On long standing in water, they gradually added water and were converted to white crystals which, on heating, lost water and again acquired a bright crimson color.

The dioxime. A mixture of 1.18 g (0.005 mole) of the diketone, 1.4 g (0.022 mole) of hydroxylamine hydrochloride, 3 ml of anhydrous alcohol and 10 ml of dry pyridine was refluxed for 4 hours. After cooling, the solution was poured into 150 ml of cold water; the precipitate which came down was separated, washed with water and dried. We obtained 1.3 g (98%) of the dioxime of 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4, which consisted of white crystals which were very soluble in alcohol and pyridine, but insoluble in water; its m.p. was 182.5-183° (from dilute alcohol).

Found %: N 10.39, 10.50. $C_{14}H_{22}O_3N_2$. Calculated %: N 10.52.

III. Preparation of 2,2,5,5-bis-tetramethylenetetrahydrofuranone-3

80 g (0.41 mole) of bis-(1-hydroxycyclopentyl)-acetylene* and 100 ml of water were placed in a liter, three-necked flask with a stirrer, reflux condenser and dropping funnel; the mixture was heated to boiling, and 33 g of mercury sulfate was added in portions during 30 minutes. After completion of the vigorous reaction, the heating was continued for 15 hours more. After cooling, the reaction product was extracted with ether; the ether extracts were treated as described previously [1].

After removal of the ether, the residue was vacuum distilled twice. We obtained 47 g (59%) of 2,2,5,5-bis-tetramethylenetetrahydrofuranone-3, which was a colorless, viscous liquid, insoluble in water, but soluble in ether and alcohol:

B.p. 111.5-112° (9 mm), n_D^{20} 1.4855, d_4^{20} 1.0446, MR_D 53.35. $C_{12}H_{18}O_2$. Calculated 52.67.

It was not described in the literature.

Found %: C 74.14, 74.20; H 9.51, 9.49. $C_{12}H_{18}O_2$. Calculated %: C 74.19; H 9.34.

The semicarbazone was obtained from 1 g of the ketone in 5 ml of pyridine, and 1.3 g of semicarbazide hydrochloride in 5 ml of water. The yield was quantitative; the m.p. was 149.5-150° (from dilute alcohol).

Found %: N 16.83, 16.84. $C_{13}H_{21}O_2N_3$. Calculated %: N 16.73.

The thiosemicarbazone was obtained by an analogous method from 1 g of the ketone and 1.5 g of thiosemicarbazide hydrochloride. The yield was quantitative; the m.p. was 193-194° (from methyl alcohol).

Found %: N 15.43, 15.61. $C_{13}H_{21}ON_3S$. Calculated %: N 15.72.

The oxime. A solution of 1.4 g (0.015 mole) of hydroxylamine hydrochloride and 1.2 g of sodium hydroxide in 4 ml of water was added to a solution of 1.94 g (0.01 mole) of the ketone in 10 ml of alcohol. The mixture was boiled under reflux for 2 hours. The precipitate which came down after cooling was separated and washed with water. The yield was quantitative; the m.p. was 59° (from dilute alcohol).

Found %: N 7.01, 7.00. $C_{12}H_{19}O_2N$. Calculated %: N 6.89.

4-Benzylidene-2,2,5,5-bis-tetramethylenetetrahydrofuranone-3

1.94 g (0.01 mole) of the ketone and 1.06 g (0.01 mole) of benzaldehyde were dissolved in 5 ml of alcohol, and 15 drops of a 25% solution of sodium hydroxide was added to the mixture. The precipitate which came down after 6 days of standing was separated and dried. The yield was 1.2 g (43%); the m.p. was 97.5-98° (from alcohol).

Found %: C 80.89, 80.73; H 7.92, 8.11. $C_{19}H_{22}O_2$. Calculated %: C 80.82; H 7.86.

IV. Preparation of 2,2,5,5-bis-tetramethylenetetrahydrofurandione-3,4

28 g (0.25 mole) of selenium dioxide, 300 ml of dioxan and 10 ml of water were placed in the apparatus described above. On boiling and energetically stirring the mixture, 47 g (0.24 mole) of 2,2,5,5-bis-tetramethylene-tetrahydrofuranone-3 was added dropwise during 50 minutes, and the mixture was boiled for 12 hours more. After separation of the selenium (16 g) which precipitated, treatment of the reaction product as described previously [2] and by two subsequent vacuum distillations, we obtained 40 g (83%) of 2,2,5,5-bis-tetramethylenetetrahydrofurandione-3,4, with a b.p. of 138-140° (14 mm), which crystallized in the vessel. After recrystallization from petroleum ether it melted at 37°. It was not described in the literature.

Found %: C 69.33, 69.10; H 7.81, 7.99. $C_{12}H_{16}O_3$. Calculated %: C 69.23; H 7.74.

The substance consisted of crimson-red crystals, which were soluble in ether, alcohol, acetone, pyridine and dioxan. On long standing with water for a period of several months, it gave a white crystalline hydrate which was insoluble in water. The hydrate lost water on heating, and the substance regained its bright crimson color.

The dioxime. A mixture of 1.04 g (0.005 mole) of the diketone and 1.4 g (0.022 mole) of hydroxylamine hydrochloride, 3 ml of anhydrous alcohol and 10 ml of dry pyridine was refluxed for 4 hours. After treatment of the reaction product as described above, we obtained 1.1 g (92%) of the dioxime of 2,2,5,5-bis-tetramethylenetetrahydrofurandione-3,4; the m.p. was 199-200° (from dilute alcohol). The white crystalline substance was insoluble in water, but soluble in alcohol and in pyridine.

* Bis-(1-hydroxycyclopentyl)-acetylene was obtained by the Iotsich reaction by reaction of cyclopentanone with acetylenedimagnesium bromide; the m.p. was 109-110° [5, 6].

Found %: N 11.59, 11.61. $C_{12}H_{18}O_3N_2$. Calculated %: N 11.76.

SUMMARY

The oxidation by selenium dioxide of the bis-pyran ketones of the tetrahydrofuran series was a convenient method of production of the corresponding 3,4-diketones. The 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4 and 2,2,5,5-bis-tetramethylenetetrahydrofurandione-3,4, described in the present work, consisted of bright, crimson-colored crystals, which formed white hydrate crystals on standing with water.

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* See Consultants Bureau Translation, page 191.

CONJUGATED SYSTEMS

LVII. CONDENSATION OF VINYLPYRIDINE WITH DIENE HYDROCARBONS

A. A. Petrov and V. Dyudvig

Among other reactive vinyl compounds the vinylpyridines have attracted attention to themselves in recent years, especially the more available α-vinylpyridine [1]. The mutual influence of the ethylene bond and pyridine ring in this compound leads to the appearance of a highly electrophilic terminal carbon atom in the vinyl grouping, as a result of which α-vinylpyridine readily combines with many nucleophilic reagents (alcohols, amines, hydrocyanic acid, etc.) [2], and also enters into the homocyclization reaction with dienes (the "diene synthesis" reaction) [3-5]. α-Vinylpyridine is reminiscent of acrylonitrile in its reactivity.

We set ourselves the task of making a more detailed study of the homocyclization of α-vinylpyridine with various diene hydrocarbons. Up to the present study only the reactions of α-vinylpyridine with divinyl [5], isoprene [4], diisopropenyl [5] and β-phenylbutadiene [3] have been described. However, the condensation products were obtained in small yield (30-40%) and were insufficiently characterized.

Our experiments revealed that at 160-170°, α-vinylpyridine readily condenses with divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene and cyclohexadiene with the formation of the corresponding hydroaromatic derivatives of pyridine in 50-60% yield. α-Vinylpyridine failed to react with cyclooctatetraene under these conditions.

The formation of two products in each case could be expected as the result of reacting α-vinylpyridine with piperylene and isoprene. The structure of the condensation product from α-vinylpyridine and isoprene was proved earlier by its conversion into α-(p-tolyl)pyridine [4]. The condensation product from piperylene and α-vinylpyridine proved to be identical with the substance obtained by the action of α-pyridyllithium on o-bromotoluene. On the basis of this it was assigned the structure of α-(2-methyl-3-cyclohexenyl)pyridine. As a result, in both cases the addition proceeded in accord with the electron configuration of the components.

The α-cyclohexenylpyridines are oily liquids with a specific unpleasant and persistent odor. They are readily soluble in organic solvents and difficultly soluble in water.

The constants of the pyridine derivatives obtained by us are given in the table.

From the table it is possible to make some conclusions relative to the influence of structure on the physical properties.

1) The introduction of each new methyl group in the cyclohexene ring, not at the double bond, raises the boiling point by 7-9°. The appearance of a methyl group at the double bond raises the boiling point even more (by 13-16°).

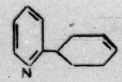
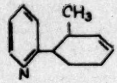
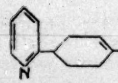
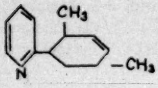
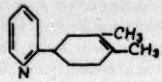
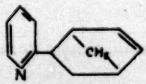
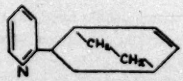
2) The isomers with methyl groups at the double bond also have greater densities and refractive indices.

3) For all of the substances the found molecular refraction is considerably lower than the calculated value. Such a deviation is characteristic for pyridine, its homologs and certain derivatives.

On the example of α-cyclohexenylpyridine we investigated some of the chemical properties of this series of compounds.

The oxidation of α-cyclohexenylpyridine with permanganate gave picolinic acid. Its dehydrogenation over platinum gave α-phenylpyridine in small yield, which was identified as the picrate. Hydrogenation of the substance over colloidal palladium proceeded very slowly and only one mole of hydrogen was absorbed. The reaction product proved to be α-cyclohexylpyridine. Bromination in chloroform apparently gives at first the normal bromine addition product at the double bond. However, on removal of the chloroform this product is transformed into the hydrobromide salt of bromocyclohexenylpyridine. A crystalline methiodide is obtained when the substance is heated with methyl iodide.

TABLE

Substance	B.p. of substance (20 mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	M.p. of picrate
	125°	1.0150	1.5444	49.55	50.67	114°
	77-80 (0.5 mm)	–	–	–	–	114-115 [5]
	132-133	0.9958	1.5374	54.37	55.29	110-111
	141-141.5	0.9956	1.5382	54.45	55.29	104-108
	103-104 (6 mm)	0.9961	1.5390	54.49	55.29[4]	–
	139-142	0.9784	1.5284	58.98	59.81	–
	154	0.9937	1.5410	59.22	59.81	101
	128-130 (6 mm)	–	–	–	–	106.5-107.5 [5]
	133-134	1.0621	1.5578	51.95	53.09	142-143
	150-154*	1.0692	1.5590	56.31	57.71	123

All of the condensation products readily react with picric acid to give (in all cases except one) well-crystallized salts.

The performed transformations are depicted (for divinyl) in the form of the scheme [see top of next page].

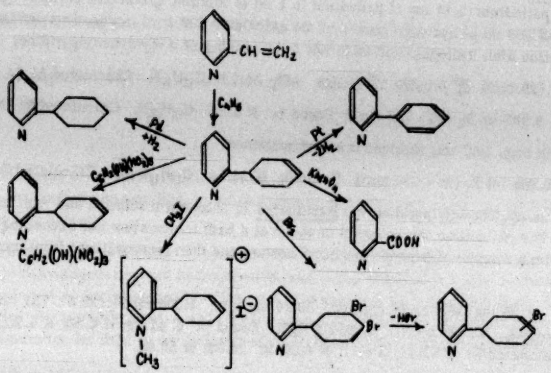
EXPERIMENTAL

α-Vinylpyridine was prepared from β-hydroxyethylpyridine by distillation with a small amount of KOH. The hydroxyethylpyridine was prepared in the usual manner – by the condensation of α-picoline with formaldehyde [1, 6]. The constants of β-hydroxyethylpyridine are:

B.p. 128° (20 mm), d_4^{20} 1.0966, n_D^{20} 1.5380. MR_D 35.13. C_7H_9ON. Calculated 34.07.

Literature data [6]: b.p. 110-114° (10 mm), n_D^{20} 1.5374.

* The wide boiling range was taken on account of the small amount of substance.



The constants of α-vinylpyridine are:

B.p. 60° (20 mm), d_4^{20} 0.9770, n_D^{20} 1.5518. MR_D 34.43. C_7H_7N. Calculated 34.40.

Literature data [1]: b.p. 60° (17 mm), 69-71° (30 mm); d_4^{21} 0.9661, n_D^{20} 1.5495.

The diene hydrocarbons were obtained by the methods described in previous communications. For reaction we took them in 20% excess, and in the case of piperylene, dipropenyl and cyclohexalene in 50% excess (based on the approximate amount of unreactive cis-form, and in the last case on the amount of cyclohexene). The reaction was run in xylene.

Condensation of α-vinylpyridine with divinyl. A mixture of 16 g of vinylpyridine, 20 ml of divinyl and 50 ml of xylene was heated in sealed glass tubes at 170° for 10 hours. The reaction product (after removal of most of the xylene at atmospheric pressure) was distilled in vacuo to give 14 g of α-cyclohexenyl pyridine. Yield 60%. The constants of this and of the other condensation products are given in the table.

38.50 mg sub.: 117.00 mg CO_2; 28.50 mg H_2O. 22.05 mg sub.: 1.764 ml N_2 (25°, 742 mm). 0.2010 g sub.: 14.1 g benzene: Δt 0.465°. Found %: C 83.08; H 8.28; N 8.95. M 159.8. $C_{11}H_{13}N$. Calculated %: C 82.97; H 8.23; N 8.80. M 159.2.

The picrate was obtained in the usual manner from the substance. It was recrystallized, as were all of the other picrates described below, from ethyl alcohol. The melting point is given in the table.

21.55 mg sub.: 2.813 ml N_2 (25°, 746 mm). Found %: N 14.67. $C_{17}H_{16}O_7N_4$. Calculated %: N 14.43.

The heating of 2 g of α-cyclohexenylpyridine with methyl iodide at 100° for 2 hours in a sealed glass tube gave 1.5 g of crystalline methiodide with m.p. 188° (from alcohol).

35.0 mg sub.: 61.1 mg CO_2; 17.1 mg H_2O. 37.05 mg sub.: 1.568 ml N_2 (24°, 744 mm). Found %: C 47.64; H 5.47; N 4.76. $C_{12}H_{16}NI$. Calculated %: C 47.86; H 5.35; N 4.65.

α-Cyclohexenylpyridine (2.5 g) was oxidized with a 4% potassium permanganate solution. After filtration, the solution was evaporated in vacuo, neutralized with dilute H_2SO_4, and again evaporated in vacuo. The residue was treated with alcohol. To the alcohol solution, filtered from precipitated salts and evaporated in vacuo, was added copper acetate. The obtained copper salt of picolinic acid was filtered and then treated in water suspension with hydrogen sulfide. Picolinic acid with m.p. 136-137° was isolated from the filtered and evaporated solution. The same melting point is given for this acid in the literature [7].

For the dehydrogenation of α-cyclohexenylpyridine 4 g of the condensation product was passed twice over platinized charcoal at 400-450°. The condensate fraction boiling above 130° at 20 mm was treated in alcohol solution with picric acid to give the picrate of α-phenylpyridine with m.p. 170-171°. The m.p. given in the literature for this compound is 175° [6].

11.85 mg sub.: 1.609 ml N_2 (23°, 754 mm). Found %: N 14.64. $C_{17}H_{18}O_7N_4$. Calculated %: N 14.58.

The hydrogenation for 20 hours of 4.26 g of α-cyclohexenylpyridine in 35 ml of methyl alcohol with the aid of 10 ml of colloidal palladium (1.14 mg of palladium in 1 ml of solution, protective colloid – gum arabic) resulted in the absorption of 568 ml of hydrogen instead of the calculated 599.4 ml (reduced to standard conditions). From the alcohol solution after hydrogenation there was isolated 3.8 g of α-cyclohexylpyridine:

B.p. 124-124.5° (20 mm), d_4^{20} 0.9928, n_D^{20} 1.5295. MR_D 50.13. $C_{11}H_{15}N$. Calculated 51.14.

12.06 mg sub.: 0.907 ml N_2 (26°, 755 mm). Found %: N 8.53. $C_{11}H_{15}N$. Calculated %: N 8.69.

The picrate with m.p. 104° was obtained from the substance.

6.26 mg sub.: 0.804 ml N_2 (26°, 758 mm). Found %: N 14.14. $C_{17}H_{18}O_7N_4$. Calculated %: N 14.35.

Three grams of α-cyclohexenylpyridine was brominated in chloroform solution and with ice cooling by bromine in 20% excess. The chloroform was removed in vacuo at a bath temperature not exceeding 30°. The solid residue was treated with a mixture of benzene and ethyl acetate and then recrystallized from methanol. Yield 1.1 g, m.p. 182-183°.

31.50 mg sub.: 48.35 mg CO_2; 12.75 mg H_2O. 33.80 mg sub.: 1.294 ml N_2 (28.5°, 751 mm). 0.1226 g sub.: 3.85 ml 0.1 N $AgNO_3$. 0.0836 g sub.: 0.0982 g AgBr. Found %: C 41.89; H 4.53; N 4.28; Br' 25.10; Br 49.98. $C_{11}H_{13}NBr_2$. Calculated %: C 41.41; H 4.11; N 4.39; Br' 25.04; Br 50.09.

Condensation of α-vinylpyridine with piperylene. Under the same reaction conditions from 15 g of vinylpyridine and 15 g of piperylene there was obtained 12 g (49%) of condensation product. The same product was also obtained by the reaction of o-bromotoluene with α-pyridyllithium.

35.55 mg sub.: 108.25 mg CO_2; 27.75 mg H_2O. 28.80 mg sub.: 2.097 ml N_2 (28.5°, 743 mm). Found %: C 83.10; H 8.73; N 8.06. $C_{12}H_{15}N$. Calculated %: C 83.19; H 8.73; N 8.08.

Picrate: 26.50 mg sub.: 3.352 ml N_2 (26°, 755 mm). Found %: N 14.34. $C_{18}H_{18}O_7N_4$. Calculated %: N 13.93.

Condensation of α-vinylpyridine with isoprene. From 14 g of vinylpyridine and 12 g of isoprene there was obtained 11.5 g (50%) of condensation product and 7.7 g of polymer.

10.07 mg sub.: 0.725 ml N_2 (26°, 756 mm). 10.55 mg sub.: 0.768 ml N_2 (25.5°, 757 mm). Found %: N 8.18, 8.29. $C_{12}H_{15}N$. Calculated %: N 8.08.

Picrate: 10.05 mg sub.: 1.244 ml N_2 (26.5°, 757 mm). 8.47 mg sub.: 1.053 ml N_2 (26°, 757 mm). Found %: N 14.05, 14.14. $C_{18}H_{18}O_7N_4$. Calculated %: N 13.93.

Condensation of α-vinylpyridine with dipropenyl. From 10.5 g of vinylpyridine and 15 g of dipropenyl there was obtained 6 g (32%) of condensation product.

32.32 mg sub.: 98.75 mg CO_2; 26.85 mg H_2O. 15.60 mg sub.: 1.029 ml N_2 (25°, 751 mm). Found %: C 83.38; H 9.29; N 7.47. $C_{13}H_{17}N$. Calculated %: C 83.37; H 9.15; N 7.48.

The picrate of the substance failed to crystallize.

Condensation of α-vinylpyridine with diisopropenyl. From 10.5 g of vinylpyridine and 10 g of diisopropenyl there was obtained 11 g (60%) of condensation product and 5.2 g of polymer.

36.30 mg sub.: 110.70 mg CO_2; 29.70 mg H_2O. 29.90 mg sub.: 1.980 ml N_2 (30°, 743 mm). Found %: C 83.22; H 9.16; N 7.29. $C_{13}H_{17}N$. Calculated %: C 83.37; H 9.15; N 7.48.

Picrate: 27.00 mg sub.: 3.195 ml N_2 (26°, 755 mm). Found %: N 13.42. $C_{19}H_{19}O_7N_4$. Calculated %: N 13.46.

Condensation of α-vinylpyridine with cyclopentadiene. From 10.5 g of vinylpyridine and 8 g of cyclopentadiene there was obtained 12.4 g (66.7%) of condensation product.

40.81 mg sub.: 125.60 mg CO_2; 28.15 mg H_2O. 18.35 mg sub.: 1.372 ml N_2 (27.5°, 742 mm). Found %: C 83.99; H 7.72; N 8.29. $C_{13}H_{13}N$. Calculated %: C 84.17; H 7.65; N 8.18.

Picrate: 23.80 mg sub.: 2.940 ml N_2 (25°, 747 mm). Found %: 13.91. $C_{19}H_{16}O_7N_4$. Calculated %: N 14.00.

Condensation of α-vinylpyridine with cyclohexadiene. From 10.5 g of vinylpyridine and 12 g of cyclohexadiene (obtained from dibromocyclohexane by distillation with quinoline) under the usual conditions there was obtained a total of 0.9 g of condensation product.

35.20 mg sub.: 108.20 mg CO_2; 25.70 mg H_2O. 18.35 mg sub.: 1.235 ml N_2 (28°, 742 mm). Found %: C 83.88; H 8.17; N 7.45. $C_{13}H_{15}N$. Calculated %: C 84.28; H 8.16; N 7.56.

Picrate: 21.90 mg sub.: 2.675 ml N_2 (27°, 747 mm). Found %: N 13.66. $C_{19}H_{18}O_7N_4$. Calculated %: N 13.52.

SUMMARY

1. The condensation of α-vinylpyridine with divinyl, piperylene, isoprene, dipropenyl, diisopropenyl, cyclopentadiene and cyclohexadiene was studied, in which connection it was established that normal homocyclization products are formed in all cases.

2. On the example of α-cyclohexenylpyridine the behavior of the obtained products to the action of oxidizing agents, catalytic dehydrogenation and hydrogenation, and to the action of bromine in chloroform solution, was studied. The oxidation of α-cyclohexeneylpyridine with permanganate gave picolinic acid. Dehydrogenation over platinum gave α-phenylpyridine in small yield. Hydrogenation with the aid of colloidal palladium gave α-cyclohexylpyridine. Bromination resulted in the isolation of the hydrobromide of bromocyclohexenylpyridine as the final reaction product.

3. Characteristic crystalline picrates were obtained for most of the condensation products and for one the methiodide was obtained.

4. As a result of the present study the analogous behavior of α-vinylpyridine and acrylonitrile as regards the homocyclization reaction with diene hydrocatbons was established.

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CONJUGATED REACTIONS FOR THE ADDITION OF HALOGENS TO OLEFINS

IV. PREPARATION OF THE β-HALOETHYL ESTERS OF FORMIC, ACETIC, CHLOROACETIC AND TRICHLOROACETIC ACIDS

A. I. Titov, F. L. Maklyaev, and V. G. Kuzmin

The synthesis of β-haloethyl esters of carboxylic acids is realized by reaction of the halogen and ethylene in the corresponding acid medium in accord with the scheme:

$$X_2 + CH_2{=}CH_2 + RCOOH \longrightarrow XCH_2{-}CH_2OCOR + HX. \quad (1)$$

Together with the conjugation reaction depicted by equation (1) with involvement of the carboxylic acid, there also occurred the formation of the dihaloethane $XCH_2{-}CH_2X$.

According to our postulation [1], both reactions proceed through the primary interaction of the electrophilic halogen molecule with the mobile π-bond electrons.

$$X{-}X + \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \rightleftharpoons \overset{+\delta}{X}{-}X \leftarrow \begin{matrix} +\delta CH_2 \\ | \\ CH_2 \end{matrix} \quad (2)$$

Due to the spatial availability and electrophilic nature of the carbon atoms, the complex is a vigorous alkylation agent. Such a complex with the anions $RCOO^-$ and X^- of the acids themselves or of their salts leads to the formation of the following reaction products:

$$\overset{+\delta}{X}{-}X \leftarrow \begin{matrix} +\delta CH_2 \\ | \\ CH_2 \end{matrix} \xrightarrow{RCOO^-} X^- + X{-}CH_2{-}CH_2{-}OOCR \quad (3)$$

$$\xrightarrow{X^-} X^- + X{-}CH_2{-}CH_2{-}X \quad (4)$$

(X designates the halogen involved in the reaction)

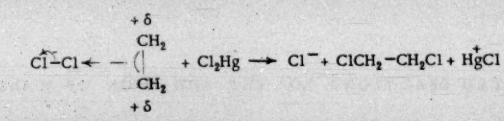
An increase in the concentration of halogen ion or of hydrogen halide should cause an undesirable increase in the amount of dihaloethane formed in accord with equation (4), which was confirmed when the preparation of β-chloroethyl acetate by this method was studied. A yield of the ester up to 38.3% of the theoretical was obtained when the conjugation reaction was run under the usual conditions. Preliminary saturation of the acetic acid with hydrogen chloride resulted in reduction of the yield down to 27%. The comparatively slight decrease in yield is explained by the fact that saturation with hydrogen chloride was also achieved toward the middle of the process even in the first case, due to its formation (HCl) in the conjugation reaction (1).

The addition of mercury acetate to the acetic acid made it possible markedly to increase the yield of β-chloroethyl acetate (up to 70%). The influence of the following factors can serve as an explanation for this:

1) an increase in acetate ion concentration, which served to promote reaction of the complex in accord with equation (3) with the formation of the ester;

2) a reduction in chlorine ion concentration as the result of its being bound up in mercury chloride, which reduced the possibility of its reacting in accord with equation (4);

3) the greater effectiveness of mercury acetate as an acetate ion donor, when compared to mercury chloride as a chlorine ion donor, in their reaction with the complex in accord with the equations of type (5).



(5)

Our conclusion on the relative effectiveness of these mercury salts as donors of the corresponding anions is based on a comparison of their electrolytic dissociation tendency, i.e., on their tendency to release anions to the solvent, since the cation is the same for both salts.

The preparation of β-bromoethyl acetate by the direct reaction of ethylene with a solution of bromine in acetic acid gave in our experiments an extremely small yield of the ester due to the high activity of the bromine ion and hydrogen bromide as regards reaction with the complex with the formation of dibromoethane. According to our observations [2], the activity of the bromine ion in conjugation reactions is 10-15 times that of the chlorine ion. The addition of mercury acetate made it possible to obtain β-bromoethyl acetate in excellent yield.

The reaction of chlorine with ethylene in formic acid gave β-chloroethyl formate in higher than 50% yield, in chloroacetic acid β-chloroethyl chloroacetate was obtained, and in trichloroacetic acid β-chloroethyl trichloroacetate was obtained.

EXPERIMENTAL

I. Preparation of β-chloroethyl acetate. In a 150 ml glass reactor of the earlier described type [3] was placed 63 g of glacial acetic acid (1.05 moles) and in the course of 2 hours with extremely vigorous stirring with a propeller stirrer there was admitted 19.2 liters (0.85 mole) of chlorine and 22.3 liters (0.89 mole) of ethylene. The reaction product was diluted with 100 ml of water, neutralized with strong alkali, the organic layer was separated, washed with water, and dried over calcium chloride. Fractional distillation gave the fractions: 1st 84-100°, 46.5 g; 2nd 100-140°, 3.5 g; 3rd 143-145°, 33.1 g; residue 4 g.

The 3rd fraction corresponded to β-chloroethyl acetate [4];

d_4^{17} 1.1465, n_D^{17} 1.4255, MR_D 27.35; calculated 27.19.

For the Volhard determination of chlorine a sample of the ester was heated for 3 hours with 50 ml of water in a flask under reflux and then for another 5 hours after adding 2 g of caustic.

Found %: Cl 28.5. $C_4H_7O_2Cl$. Calculated %: Cl 29.0.

When the reaction was run with 12 liters of chlorine and 14 liters of ethylene in acetic acid with the addition of mercury acetate, 32 g of the salt was introduced before the start of reaction and the same amount was added after half the amount of gases had been admitted. After washing the reaction mass with water, the organic layer was separated, dried, and fractionally distilled to give the fractions: 1st 84-100°, 11.5 g; 2nd 100-140°, 9.5 g; 3rd 140-145°, 33.8 g; residue 15 g, containing much mercury chloride.

The yield of ester, if it is assumed that its content in the 2nd fraction is 50%, is 67%, referred to the sum of both reaction products.

II. Preparation of β-bromoethyl acetate. The conjugation reaction was successfully realized only in the presence of mercury acetate. Into the reactor were successively charged 50 ml of glacial acetic acid, 40 g of mercury acetate, 30 g of bromine and then for 1 hour the mixture was saturated with stirring with 5 liters of ethylene to disappearance of color. The precipitate of mercury bromide was separated, washed with 50 ml of water and then with a small amount of diethyl ether. The filtrate was partially stratified with 30 ml of 40% sodium hydroxide solution; the organic layer was washed with soda solution and then dried over potash. The product was first distilled in vacuo to free it of mercury compounds; subsequent fractionation gave the fractions: 1st to 140°, 2.8 g; 2nd 140-154°, 2.2 g; 3rd 155-165°, 14.5 g.

The 3rd fraction almost entirely distilled at 159-164°, which closely approaches the literature data for the boiling point of β-bromoethyl acetate (162-163°), which was obtained in small yield by Ushakov and coworkers [5] by the reaction of bromine, silver acetate and ethylene in carbon tetrachloride. The yield of ester was about 80% based on the sum of the reaction products.

III. β-Chloroethyl formate was synthesized by the first variation given in section I. Into the reactor was poured 92 g of formic acid (d 1.2). At 30° and with vigorous stirring there was passed 27.5 liters (1.23 moles) of chlorine and 28 liters (1.25 moles) of ethylene; there was collected 5 liters of unabsorbed gases with an ethylene

content of 10%. After the usual treatment and distillation the following fractions were obtained: 1st 80-90°, 58.7 g; 2nd 90-129°, 3.8 g; 3rd 129-130°, 58.1 g; residue 5.5 g.

The 3rd fraction with b.p. 129-130° was β-chloroethyl formate:

d_4^{17} 1.2296, n_D^{17} 1.4288, MR_D 22.74; calculated 22.87. Found %: Cl 31.4. $C_3H_5O_2Cl$. Calculated %: Cl 31.6.

IV. Synthesis of β-chloroethyl chloroacetate and β-chloroethyl trichloroacetate. Into a melt of 100 g of trichloroacetic acid at 75° was passed about 10 liters of chlorine and 11 liters of ethylene. After treatment with 100 ml of water, washing the organic layer with soda solution, drying and distillation, the following fractions were obtained: 1st 80-90°, 32.5 g; 2nd 95-105° at 10 mm, 41.5 g (35%).

The 2nd fraction when distilled at atmospheric pressure almost completely distilled at 217°, which corresponds to the literature data for the boiling point of β-chloroethyl trichloroacetate. β-Chloroethyl chloroacetate with b.p. 197-198° was obtained in an analogous manner in about 40% yield.

SUMMARY

1. The preparation of β-haloethyl acetates by the conjugation reaction method was studied. In accord with theory it was shown that saturation of the reaction mass with hydrogen chloride decreases the relative yield of ester in favor of the formation of dichloroethane, while the addition of mercury acetate increases the yield of ester. The successful preparation of β-bromoethyl acetate is possible only in the presence of mercury acetate.

2. By the conjugation reaction method the interaction of chlorine and ethylene in formic acid gave β-chloroethyl formate, in chloroacetic acid – β-chloroethyl chloroacetate, and in trichloroacetic acid – β-chloroethyl trichloroacetate.

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THE SYNTHESIS OF α-MERCAPTOISOBUTYRALDEHYDE

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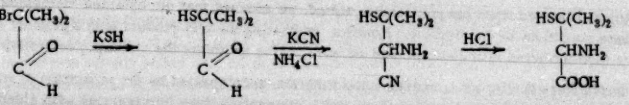
Use is made of α-bromoisobutyraldehyde [1] as the starting material in one of the known methods for the preparation of penicillamine. By the action of sodium benzylmercaptide this aldehyde is converted into α-benzylmercaptoisobutyraldehyde, which by the action of HCN and NH_3 using the Strecker method [2] is then converted into the corresponding amino nitrile, the hydrolysis of which leads to the formation of benzylmercaptopenicillamine. The latter, under the influence of sodium in liquid ammonia is converted into dimethylcysteine.

In principle it is possible to go from α-bromoisobutyraldehyde to penicillamine by a different route:



In this method the bromine is directly replaced by the mercapto group, and for this reason the step of reduction with sodium in liquid ammonia becomes unnecessary. In addition, the transition from α-mercaptoisobutyraldehyde is effected not by the action of free hydrocyanic acid and ammonia, but by the method of N. D. Zelinsky and G. L. Stadnikov [3] using KCN and NH_4Cl.

One of the starting products for the preparation of penicillamine by this method is α-mercaptoisobutyraldehyde. Our work was an attempt to synthesize this compound.

Up to now a good and simple method for the preparation of monomeric α-bromoisobutyraldehyde has failed to exist. It had been obtained either by the depolymerization of the polymer [4] or by the hydrolysis of its diethyl acetal [5-11]. However, according to the data of S. N. Danilov [12], the depolymerization of the α-bromoisobutyraldehyde polymer frequently leads to ppor results due to the cleavage of hydrogen bromide, resinification, and the formation of a polymer mixture of the unsaturated aldehyde. All of the different variations for the synthesis of α-bromoisobutyraldehyde via the hydrolysis of its diethyl acetal also fail to give good yields. A new bromination method with dioxan dibromide has been proposed by L. A. Yankovskaya and A. P. Terentyev [13], and they obtained α-bromoisobutyraldehyde in 58% yield.

Since for the conversion of α-bromoisobutyraldehyde into the mercapto derivative either prolonged heating or the use of an alkaline agent (KSH) was required, which could cause polymerization and resinification, we decided to protect the aldehyde group by converting the aldehyde into either the polymer or the acetal. The polymer of isobutyraldehyde, obtained at 0° by the action of a drop of sulfuric acid, was brominated in CCl_4 solution [12]. On attempting to introduce the mercapto group into it by heating with sodium thiosulfate by the method of V. M. Rodionov and N. N. Suvorov [14] there occurred resinification, and we were unable to obtain the mercapto derivative.

We obtained the diethyl acetal of α-bromoisobutyraldehyde by the method of Zeisel and Daniek [11], involving the bromination of a mixture of anhydrous alcohol and isobutyraldehyde in the presence of chalk. However, the attempts to obtain the diethyl acetal of α-mercaptoisobutyraldehyde by the action of NaSH on the diethyl acetal of α-bromoisobutyraldehyde failed to give positive results, and the diethyl acetal of α-bromoisobutyraldehyde was recovered unchanged from the reaction. Then it was decided to attempt the preparation of the mercaptoisobutyraldehyde by the action of KSH on the monomeric α-bromoisobutyraldehyde. Since not one of the above-described methods gave α-bromoisobutyraldehyde in sufficiently good yields, which circumstance many authors explained as being due to the harmful influence exerted by the hydrogen bromide evolved during reaction, we decided to run the bromination of isobutyraldehyde in anhydrous ether solution and in the presence of chalk to effect more complete binding of the hydrogen bromide. Under such conditions extremely pure α-bromoisobutyraldehyde is obtained in yields up to 78%, which is considerably higher than any results that have been obtained to date. The bromoaldehyde obtained in this manner fails to undergo polymerization on standing, which is in contrast to the product obtained by the depolymerization of the bromoisobutyraldehyde polymer. α-Bromoisobutryaldehyde quite

readily cleaves hydrogen bromide due to the position of the bromine at a tertiary carbon atom. Treatment of the aldehyde with a solution of 2,4-dinitrophenylhydrazine gave a product that was devoid of halogen and which analyzed high in nitrogen.

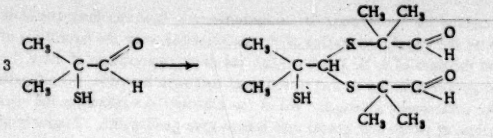
The reaction of α-bromoisobutyraldehyde with KSH was run in anhydrous ether medium. The ether solution obtained from the reaction contains the mercaptoisobutyraldehyde, which is indicated by the qualitative test with nascent nitrous acid, titration with iodine solution, and the formation of the sodium and silver mercaptides. We attempted to isolate the mercaptoaldehyde from the reaction products by converting it into the solid sodium mercaptide [15], but in the decomposition of this mercaptide with dilute sulfuric acid there occurred resinification, and we were unable to isolate the mercaptoaldehyde by this method. The distillation of the reaction products even in deep vacuum resulted in the separation of water and the formation of a yellowish oily product, which was not distillable.

It is known that mercaptans are easily oxidized even by atmospheric oxygen, in which connection the disulfide is formed and water is liberated. The disulfides are readily reduced by nascent hydrogen and other reducing agents with the formation of mercaptans. Thus, Otto and Rossing [16] converted disulfides into mercaptans by heating them with an alcoholic K_2S solution and subsequent treatment of the formed mercaptide with acid.

Since water was liberated when our product was heated, we assumed that the obtained mercaptoaldehyde was oxidized under these conditions to the disulfide. However, on heating the oily product with K_2S under the above indicated conditions there occurred resinification, and we were unable to isolate the mercapto derivative.

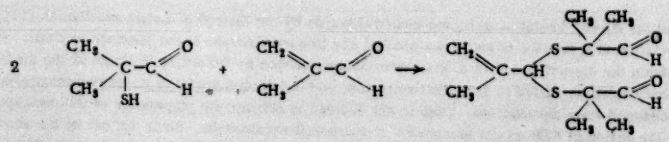
Mercapto derivatives can also suffer another transformation, accompanied by the separation of water; under the condensation influence of hydrogen halide acids or $ZnCl_2$ mercaptans enter into reaction with aldehydes and ketones, forming mercaptals. As indicated by Baumann [17, 18], mercaptals can be either crystalline or liquid; the liquid mercaptals are extremely difficult to obtain in pure form, since they undergo decomposition when distilled.

The mercaptoisobutyraldehyde contains in its structure both the aldehyde and the mercapto group, consequently its molecules can enter into reaction with each other, forming the mercaptal:



(I)

The hydrogen bromide needed for the condensation reaction is undoubtedly present both in the ether solution containing the mercaptoaldehyde, and in the oil, formed during heating, since, on the one hand, both of these products show acid to litmus and contain halogen, and on the other hand, on attempting to distil the reaction products in vacuo a substance was collected in the trap, which from the obtained data can presumably be considered to be the product of HBr cleavage from the bromoisobutyraldehyde, namely methacrylaldehyde (methacrolein). In addition to the above-indicated mercaptal, the formation of another mercaptal can be assumed, which can be obtained as the result of the condensation of the mercaptoaldehyde with methacrylaldehyde:



(II)

If from the reaction mixture, obtained in the reaction of α-bromoisobutyraldehyde with KSH, the ether is removed by suction without heating, then after removal of the ether there remains a crystalline product, which after several recrystallizations from petroleum ether is almost completely transformed into an oil. The residual crystals had m.p. 75-77°. Both the crystals and the oil gave a 2,4-dinitrophenylhydrazone with m.p. 250-252°, giving a positive reaction for sulfur (by Lassen). On attempting to recrystallize the precipitate from alcohol the crystals completely disappeared; an oil immediately separated from the solution, which also gave a 2,4-dinitrophenylhydraz-

one with m.p. 250-251°. The determination of the specific gravity, molecular weight and molecular refraction, the analysis results for the 2,4-dinitrophenylhydrazone, and also the decolorization of bromine in benzene solution, make it possible to assume that the oil is a mixture of the mercaptals of α-mercaptoisobutyraldehyde (I) and methacrylaldehyde (II), formed in accord with the above indicated schemes.

As a result, although α-mercaptoisobutyraldehyde is obtained in the reaction of KSH with α-bromoisobutyraldehyde, its isolation from the mixture of products cannot be effected, due to the ease with which it cleaves water, apparently being converted into a mixture of mercaptals.

EXPERIMENTAL

Isobutyraldehyde was obtained by the dehydrogenation of isobutyl alcohol over brass turnings at 500-550° [9].

Bromination of isobutyraldehyde polymer [12]. To 36 g of isobutyraldehyde, cooled to 0°, was added one drop of sulfuric acid. To the obtained polymer, dissolved in 50 ml of CCl_4, with cooling and stirring was added 80 g of bromine. Yield of polymer 62.4 g (82.6%). After two recrystallizations from alcohol, m.p. 125-126°. According to S. N. Danilov [12], a yield of 75% and higher; m.p. 130°.

Preparation of the mercaptoaldehyde polymer. A solution of 18.2 g of $Na_2S_2O_3 \cdot H_2O$ in 20 ml of water, 10.57 g of bromoaldehyde polymer and 45 ml of alcohol were heated for 8 hours on the water bath with stirring, then from a dropping funnel was quickly added 30.8 ml of warm 50% sulfuric acid. After addition of the sulfuric acid, the reaction mixture was cooled in a stream of CO_2. Distillation of the reaction products gave several drops of the bromoaldehyde, while the residue proved to be a not distillable and not crystallizable tar, giving a positive reaction for both sulfur and halogen.

Preparation of the diethyl acetal of α-bromoisobutyraldehyde [11]. To a well-cooled mixture of 20 g of aldehyde and 51 g of anhydrous alcohol in the presence of 25 g of $CaCO_3$ with stirring was added dropwise 14.2 ml of bromine. After standing overnight the reaction mixture was treated with soda solution, washed with water and extracted with ether. After drying and removal of the ether there was obtained on distillation 10.5 g (16.8%) of the diethyl acetal of α-bromoisobutyraldehyde with b.p. 60-62° at 8 mm.

d_4^{20} 1.1815, n_D^{20} 1.4399, MR_D 50.18. $C_8H_{17}O_2Br$. Calculated 50.20.

Literature data [11]: b.p. 87.5° (30 mm), n_D^{20} 1.4345.

Synthesis of the diethyl acetal of α-mercaptoisobutyraldehyde. A slurry of 12 g of dry NaSH in ether was added with stirring to a solution of 22 g of the diethyl acetal of α-bromoisobutyraldehyde in 30 ml of anhydrous ether. After stirring for 5 hours there was isolated 16 g of the original diethyl acetal of α-bromoisobutyraldehyde from the reaction products. The residue contained a dark tar, giving a positive test for both halogen and sulfur.

Bromination of isobutyraldehyde. A solution of 60 g of isobutyraldehyde in 500 ml of anhydrous ether and 120 g of freshly ignited and well-dried chalk were placed in an ice-salt cobled round-bottomed flask fitted with reflux condenser and dropping funnel, through which with good stirring and illumination with a strong lamp was added 42 ml of bromine in 2 hours. After adding the first drops, the addition of bromine was terminated until the color had disappeared – the initiation of reaction, after which the bromine was added without interruption, in which connection extremely rapid decolorization of the solution was observed. After all of the bromine had been added the stirring of the reaction mixture was continued for another 2 hours. The chalk precipitate was separated and washed several times with ether. After drying over Na_2SO_4 and distilling off the ether the residue was distilled in vacuo. The yield of α-bromoisobutyraldehyde with b.p. 48° at 8 mm was 108.5 g (78%).

d_4^{20} 1.4132, n_D^{20} 1.4531, MR_D 28.88. C_4H_7OBr. Calculated 28.45.

0.1465 g sub.: 0.1817 g AgBr. Found %: Br 52.76. C_4H_7OBr. Calculated %: Br 52.98.

Literature data [13]: yield 58%, n_D^{20} 1.4530.

Reaction of α-bromoisobutyraldehyde with KSH in anhydrous ether. Sixty grams of α-bromoisobutyraldehyde was added dropwise with stirring and cooling to a suspension of 35 g of KSH in 300 ml of anhydrous ether. After stirring for 5 hours the precipitate was removed and washed with ether. There was obtained 400 ml of the ether solution.

To 2 ml of this solution was added 31 ml of 0.098 N iodine solution. The back titration required 7.5 ml of 0.1 N $Na_2S_2O_3$ solution.

If it is assumed that the amount of mercapto group determined in the solution is present as the mercaptoisobutyraldehyde, then the yield of this aldehyde obtained by calculation is 43.2%. In another experiment the yield of the mercaptoaldehyde was 40%. The titration was repeated after the solution had stood for 2 days, the result remained the same.

The ether solution, containing the mercaptoaldehyde, showed an acid reaction to litmus, gave a positive test for halogen, and had a disagreeable garlic-like odor. The ether was distilled from the solution with heating on the water bath to 50°. A yellowish viscous liquid with a disagreeable odor remained in the distilling flask. On attempting to distill this liquid at 7 mm there appeared drops of water in the flask, while in the trap there was collected about 1 g of substance with a disagreeable sharp odor, devoid of sulfur, but containing traces of halogen (Beilstein test); this substance gives a silver mirror with an ammoniacal solution of silver oxide and decolorizes a solution of bromine in benzene.

d_4^{20} 0.7819, n_D^{20} 1.3880, MR_D 21.12. C_4H_8O. Calculated 20.89.

Preparation of the sodium mercaptide [15]. Small pieces of sodium were gradually added to 150 ml of the ether solution containing the mercaptoisobutyraldehyde, placed in a flask equipped with reflux condenser. The obtained white precipitate of the sodium mercaptide was filtered and separated from the small sodium pieces. The amount of mercaptide was 1.5 g. It was dissolved in water and decomposed with dilute sulfuric acid to give some brownish oily drops that floated on the surface of the solution. The solution was extracted with ether and titrated with 0.1 N iodine solution, the yield of mercapto derivative was 0.033 g, calculated as the mercaptoisobutyraldehyde.

Preparation of the silver mercaptide [20]. A dilute silver nitrate solution, containing a small amount of CH_3COONa, was added to 100 ml of the ether solution containing the mercaptoisobutyraldehyde; this first resulted in the precipitation of a black deposit, probably due to the reaction of $AgNO_3$ with various sulfur compounds. The black precipitate was filtered and to the filtrate was again added a solution of $AgNO_3$ and CH_3COONa. The slightly grayish precipitate of the silver mercaptide was washed with ether, water, again treated with hot ether, and dried in a vacuum desiccator.

0.0657 g sub.; 0.0355 g Ag. Found %: Ag 54.03. C_4H_7OSAg. Calculated %: Ag 51.18.

The high amount of silver in the mercaptide is explained by the presence in it of small amounts of the black deposit.

Reduction of the oil by treatment with K_2S [16]. Twenty-five grams of the oily liquid from the distilling flask was dissolved in alcohol and then heated with an alcohol solution of 16 g of K_2S on the water bath. The heating and stirring was continued for 4 hours. The obtained reddish-brown solution was poured into a porcelain dish and evaporated on the water bath; we were unable to isolate the mercapto derivative from the thick dark tar remaining in the dish. In another experiment on the preparation of the mercaptoisobutyraldehyde by the action of K_2S on the bromoisobutyraldehyde, on conclusion of reaction the ether was removed in vacuo without heating. The residual thick, incipiently crystalline liquid with repulsive odor was poured into a dish, where it crystallized. The obtained crystals were readily soluble in all of the ordinary solvents, and somewhat less soluble in petroleum ether and alcohol. Part of the crystals was recrystallized twice from petroleum ether; as before the obtained 0.5 g of product was a mixture of substances, since it gave a positive test for halogen, for the aldehyde and mercapto groups, and decolorized a solution of bromine in benzene; m.p. 75-77°. The 2,4-dinitrophenylhydrazone obtained from these crystals proved to be insoluble in alcohol, benzene, petroleum ether and diethyl ether; for purification it was washed with hot alcohol, and melted at 249-251°.

0.0300 g sub: 4.6 ml N_2 (20°, 762.5 mm). Found %: N 17.76. $C_{24}H_{30}O_8N_8S_2$ (2,4-dinitrophenylhydrazone of the mercaptal of α-mercaptoisobutyraldehyde). Calculated %: N 17.05. $C_{24}H_{28}O_8N_8S_2$ (2,4-dinitrophenylhydrazone of the mercaptal of methacrylaldehyde). Calculated %: N 18.09.

0.0761 g sub.: (b.p. 75-77°); 10 ml 0.0977 N iodine solution: 9.2 ml 0.1 N $Na_2S_2O_3$ (F 1.018). Found %: SH 17.73. C_4H_8OS (mercaptoisobutyraldehyde). Calculated %: SH 31.73. $C_{12}H_{22}O_2S_3$ (mercaptal of mercaptoisobutyraldehyde). Calculated %: SH 11.22.

The mother liquor, after removal of the crystals with m.p. 75-77°, on standing is transformed into a thick oil, from which the 2,4-dinitrophenylhydrazone with m.p. 250-251° was obtained. The mixed melting point with the 2,4-dinitrophenylhydrazone obtained from the crystalline product failed to show a depression. Titration with iodine solution revealed that the oil contains 14.76% of SH groups. The Beilstein test for halogen was positive. An extremely small amount of semicarbazone with m.p. 226-228° was obtained from the oil; the semicarbazone is insoluble in alcohol, benzene and petroleum ether, and like the 2,4-dinitrophenylhydrazone, it contains sulfur.

Part of the crystalline product, obtained in the reaction of the bromoisobutyraldehyde with KSH, as indicated above, was recrystallized from petroleum ether; another part was taken for recrystallization from alcohol, however, instead of crystals, an oil separated from the alcohol solution. This oil showed neutral to litmus, gave a negative test for halogen, contained the mercapto and aldehyde groups, and decolorized a solution of bromine in benzene. The 2,4-dinitrophenylhydrazone obtained from it had m.p. 250-251°, contained sulfur, and failed to depress the melting point when mixed with the 2,4-dinitrophenylhydrazone obtained from the crystalline product.

d_4^{20} 1.1337, n_D^{20} 1.5033, MR_D 75.91, 0.1428 g sub.: 16.347 g benzene: Δt 0.15°. Found: M 291.

Molecular weight of the mercaptal of α-mercaptoisobutyraldehyde 293, MR_D 80.07. Molecular weight of the mercaptal of methacrylaldehyde 259, MR_D 71.91.

SUMMARY

1. A method was developed for the preparation of α-bromoisobutyraldehyde, making it possible to increase the yield up to 78%.

2. The reaction of α-bromoisobutyraldehyde with KSH in ether solution was studied.

3. It was shown that the ether solution obtained in this reaction apparently contains α-mercaptoisobutyraldehyde, the presence of which was demonstrated by the preparation of the corresponding silver mercaptide.

4. It can be assumed with considerable probability that in the reaction of KSH with α-bromoisobutyraldehyde the hydrogen bromide cleaved from this aldehyde results in the formation of a mixture of α-mercaptoisobutyraldehyde and methacrylaldehyde mercaptals.

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* See Consultants Bureau Translation, page 1639.

INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XIII. REACTION OF THE ETHYL ESTER OF β,β'-PENTAMETHYLENEGLYCIDIC ACID WITH p-TOLUIDINE, o-TOLUIDINE AND p-ANISIDINE

V. F. Martynov and N. I. Larina

The reaction of the ethyl ester of β,β'-pentamethyleneglycidic acid with aniline was described in one of the previous reports [1]. The present work is a continuation of this investigation.

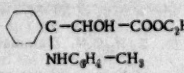
The ease of opening the oxide ring of the glycidic acids is determined not only by their structure, but also by the nature of the reagent reacting. If we limit the consideration to the amines, then two factors play an essential role here – the basicity of the amine and the steric hindrance arising at the moment of the reaction. The first factor facilitates the course of the reaction, but the second, on the other hand, impedes it. The toluidines have a greater basicity than does aniline, but on the other hand, it is necessary to expect considerable steric hindrances with o-toluidine.

Our investigations completely confirmed this assumption. p-Toluidine added under appreciably less rigid conditions than did aniline. Heating to 150-160° was necessary in order to carry out the reaction, whereas for aniline the optimum reaction temperature was 170-180°. An attempt to carry out the reaction with p-toluidine at the same temperature as for aniline, led to a product with an extremely indefinite boiling point, which clearly indicated its heterogeneity, and consequently, also indicated the different direction of the reaction.

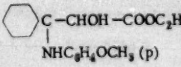
o-Toluidine, as also was to be expected, reacted with the indicated glycidic ester much more difficultly than did p-toluidine and even aniline. Heating in a sealed tube at 170-180° did not lead to obtainment of a reaction product. In order to bring about the reaction, it was found to be necessary to boil the mixture of components under reflux for a rather long time (30 hours), and even then the yield of reaction product was extremely low, 10% altogether.

As to the reaction of glycidic ester with p-anisidine, it could be expected that it proceeds less vigorously than with p-toluidine, but more vigorously than with aniline. However, it was found that p-anisidine reacts more difficultly than does aniline, which can evidently be explained by the fact that, of the two effects which the methoxy group has on the aromatic nucleus, the I-effect prevailed in the present case.

As a result of the reaction of three aromatic amines with the ethyl ester of β,β'-pentamethyleneglycidic acid, three products were obtained, to which, on the basis of a previous experiment and proof, which is cited again and described below, we gave the formulas of the ethyl ester of α-hydroxy-β-(p-toluidino)-cyclohexylpropionic acid (I), the ethyl ester of α-hydroxy-β-(o-toluidino)-cyclohexylpropionic acid (II) and the ethyl ester of α-hydroxy-β-(p-anisidino)-cyclohexylpropionic acid (III).



(I, II)



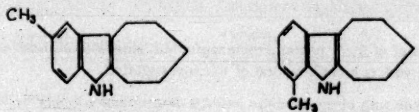
(III)

The main purpose of our work was not so much the investigation of the reaction of the aromatic amines with the ethyl ester of β,β'-pentamethyleneglycidic acid, as the study of the feasibility of the synthesis of an indole structure, starting from the addition compounds which were obtained.

The conversion of the addition compound of aniline and the ethyl ester of β,β'-pentamethyleneglycidic acid to 2,3-pentamethyleneindole was described earlier [1]. This was the first instance of the application of the new method of synthesis of indoles to the production of an indole homolog containing a seven-membered ring. In the present work we attempted to synthesize a series of compounds to extend the knowledge of this group of organic compounds, of which only one representative is known.

For this purpose we subjected the above-indicated addition compounds to the action of concentrated sulfuric acid with heating; in addition, as also was to be expected on the basis of previous works, the formation of carbon monoxide was observed, which, as is known, is peculiar to the α-hydroxy acids. This seemed to be sufficient proof of the correctness of the formulas written above. After such a cleavage the molecule fragments should be stabilized as to conversion to the corresponding homblog and derivative of 2,3-pentamethyleneindole, according to a scheme published earlier [1].

Actually, from the ethyl ester of α-hydroxy-β-(p-toluidino)-cyclohexylpropionic acid we obtained a quantitative yield of a compound to which, on the basis of previous investigation [1] and analytical data, we could properly attribute the structure of 2,3-pentamethylene-5-methylindole (IV).



(XX) (IX)

The ethyl ester of α-hydroxy-β-(o-toluidino)-cyclohexylpropionic acid decomposed under the action of sulfuric acid not so smoothly as did the preceding. In this case strong resinification was observed, which impeded the formation of the reaction product, but nevertheless we obtained a crystalline compound to which, on these same bases, we attributed the structure of 2,3-pentamethylene-7-methylindole (V).

It is necessary to remark that smooth decomposition by the action of sulfuric acid, without apparent resinification of the addition compounds of aromatic amines and glycidic acids, was observed only for crystalline, and therefore, easily purified compounds. This suggests that resinification proceeds because of impurities, which for the liquid products cannot be removed completely by ordinary distillation, even if repeated. The ethyl ester of α-hydroxy-β-(p-anisidino)-cyclohexylpropionic acid, was still decomposed by the action of sulfuric acid, with the formation of carbon monoxide, at the same temperature as for the above-described esters; however, we did not obtain the conversion product, whith may be 2,3-pentamethylene-5-methoxy (or hydroxy)indole. After completion of the reaction and decomposition of the reaction mixture with water, we observed the formation of a dark-green, resinous compound, which was not closely investigated.

EXPERIMENTAL

Reaction of the ethyl ester of β,β'-pentamethyleneglycidic acid with p-toluidine. 50 g of the ethyl ester of β,β'-pentamethyleneglycidic acid (n_D^{20} 1.4600, d_4^{20} 1.0529) in a mixture with 30 g of p-toluidine (mole for mole by calculation) was heated in a sealed ampoule for 10 hours at 150-160°.

On vacuum distillation the ethyl ester of α-hydroxy-β-(p-toluidino)-cyclohexylpropionic acid distilled at 146-147° (1 mm).

16 g (20%) of a very viscous, greenish-yellow liquid was obtained. The ethyl ester of α-hydroxy-β-(p-toluidino)-cyclohexylpropionic acid crystallized after two weeks. After recrystallization from ligroin, colorless, stable crystals, somewhat suggestive of the crystals of sodium chloride, with a m.p. of 59-60°, were obtained.

0.2410 g sub.: 10.5 ml N_2 (19°, 772 mm). Found %: N 5.10. $C_{17}H_{25}O_2N$. Calculated %: N 4.81.

Reaction of the ethyl ester of α-hydroxy-β-(p-toluidino)-β-cyclohexylpropionic acid with concentrated sulfuric acid. 2 g of the crystalline ethyl ester of α-hydroxy-β-(p-toluidino)-β-cyclohexylpropionic acid, in a mixture with 8 ml of concentrated sulfuric acid, was heated on an open electric plate in a small round-bottomed flask with frequent shaking and stirring with the thermometer which was placed in the reaction mixture. In the slightly yellowish reaction substance at a temperature of about 100°, the formation of carbon monoxide bubbles began, which became very intense at 110°. After that, when the evolution of carbon monoxide had ceased completely, the hot reaction mixture was poured onto ice. The 2,3-pentamethylene-5-methylindole which formed at this time was filtered off, washed with water, and dried; the yield was quantitative. After recrystallization from aqueous alcohol, flaky, almost colorless crystals with a m.p. of 127-128° were obtained.

The picrate consisted of claret-cinnamon colored needles with a m.p. of 149-150°.

0.1178 g sub.: 7 ml N_2 (19°, 758.8 mm). Found %: N 6.90 $C_{14}H_{17}N$. Calculated %: N 7.00.

Reaction of the ethyl ester of β,β'-pentamethyleneglycidic acid with o-toluidine. 32 g of the ethyl ester of β,β'-pentamethyleneglycidic acid, in a mixture with 19 g of o-toluidine (mole for mole), was refluxed on Wood's alloy until slight boiling of the reaction mixture. In order to avoid getting moisture into the reaction zone, the upper end of the reflux condenser was connected to a Tishchenko bottle which contained sulfuric acid. The heating was continued intermittently for 30 hours, and the reaction substance darkened strongly.

The reaction product – the ethyl ester of α-hydroxy-β-(o-toluidino)-β-cyclohexylpropionic acid – was separated by vacuum distillation of the reaction mixture. It distilled at 140-146° (1 mm) and was a viscous, yellow liquid. 5 g (10%) of the substance was obtained.

0.2247 g sub.: 9.4 ml N_2 (18°, 773.2 mm). Found %: N 4.92. $C_{17}H_{25}O_3N$. Calculated %: N 4.81.

Reaction of the ethyl ester of α-hydroxy-β-(o-toluidino)-β-cyclohexylpropionic acid with concentrated sulfuric acid. 1 g of the ethyl ester of α-hydroxy-β-(o-toluidino)-β-cyclohexylpropionic acid was mixed with 3 ml of concentrated sulfuric acid. The reaction mixture was heated in a small flask on the open flame, with frequent shaking. The temperature was checked with a thermometer, which was placed in the reaction substance. Mutual solution of the components of the mixture took place on heating, and the whole mass darkened. At about 100° the evolution of bubbles of carbon monoxide began, which became rather intense at 105-110°. After completion of the evolution of carbon monoxide the dark reaction substance was poured onto ice. 2,3-Pentamethylene-7-methylindole precipitated as a fine, resinous substance. The 2,3-pentamethylene-7-methylindole became harder and more brittle on neutralization of the acid with alkali; it was pulverized and washed with water. After recrystallization from aqueous alcohol, a low yield of flaky crystals with a m.p. of 103-104° was obtained.

The picrate consisted of dark-cinnamon colored needles with a m.p. of 119-120°.

9.475 mg sub.: 0.58 ml N_2 (20°, 763.7 mm). Found %: N 6.90. $C_{14}H_{17}N$. Calculated %: N 7.00.

Reaction of the ethyl ester of β,β'-pentamethyleneglycidic acid with p-anisidine. 30 g of the ethyl ester of β,β'-pentamethyleneglycidic acid in a mixture with 20 g of p-anisidine (mole for mole) was heated in a sealed ampoule at 170-180° for 10 hours.

The reaction product – the ethyl ester of α-hydroxy-β-(p-anisidino)-β-cyclohexylpropionic acid – after two distillations was a viscous, greenish-yellow liquid with a b.p. of 179-181° (0.5 mm). 10 g (21%) of the substance was obtained:

d_4^{20} 1.1419, n_D^{20} 1.543, MR_D 84.74; calculated 83.33.

0.1768 g sub.: 7 ml N_2 (21°, 771.4 mm). Found %: N 4.62. $C_{17}H_{25}O_4N$. Calculated %: N 4.56.

SUMMARY

1. The reaction of the ethyl ester of β,β'-pentamethyleneglycidic acid with o- and p-toluidine and p-anisidine was studied. It was shown that by the action of the indicated reagents the oxide ring of glycidic acid was opened from the side of the β-carbon atom.

2. The following, which were not described in the literature were obtained and characterized: the ethyl ester of α-hydroxy-β-(p-toluidino)-β-cyclohexylpropionic acid, the ethyl ester of α-hydroxy-β-(o-toluidino)-β-cyclohexylpropionic acid, and the ethyl ester of α-hydroxy-β-(p-anisidino)-β-cyclohexylpropionic acid.

3. The conversion of the ethyl ester of α-hydroxy-β-(p-toluidino)-β-cyclohexylpropionic acid to 2,3-pentamethylene-5-methylindole, and of the ethyl ester of α-hydroxy-β-(o-toluidino)-β-cyclohexylpropionic acid to 2,3-pentamethylene-7-methylindole was carried out. Neither of the indoles indicated were described in the literature.

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* See Consultants Bureau Translation, page 2121.

ACID HALIDES OF ALDEHYDE ACIDS

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Until the present time the acid chlorides of the simplest aldehyde acids remained unknown. As was found, the reaction of the dimethylacetal of formylacetic acid with thionyl chloride leads to the acid chloride of the dimethylacetyl of formylacetic acid (III) with a yield of 60% (b.p. 65-67° at 12 mm).

$$(CH_3O)_2CHCH_2COOR \longrightarrow (CH_3O)_2CHCH_2COOH \longrightarrow (CH_3O)_2CHCH_2COCl$$

(I) (II) (III)

The methyl ester of the dimethylacetal of formylacetic acid was obtained by the formylation of ethyl acetate, and subsequent acetalization of the sodium derivative with a methanol solution of HCl [1, 2].

$$CH_3COOC_2H_5 + HCOOCH_3 \xrightarrow{CH_3ONa} \underset{CHONa}{\overset{CHCOOC_2H_5}{\|}} \xrightarrow[HCl]{CH_3OH} (CH_3O)_2CHCH_2COOCH_3.$$

The corresponding acid (II) was obtained with alcoholic alkali.

Similarly, the dimethylacetal of formylchloroacetic acid was obtained from methyl chloroacetate [3]; however, by the action of an equivalent quantity of thionyl chloride on this acid, cleavage of the alcohol molecule took place with the formation of α-chloro-β-methoxyacrylic acid (IV), with a m.p. of 172-174°. On heating the dimethylacetal of formylchloroacetic acid with an excess of thionyl chloride, a 65% yield of the acid chloride of α-chloro-β-methoxyacrylic acid (V) (b.p. 75-78° at 2 mm) was obtained. An 83% yield of this same acid chloride was obtained from acid (IV).

$$(CH_3O)_2CHCHClCOOH \xrightarrow{SOCl_2} \underset{(IV)}{CH_3OCH{=}CCl{-}COOH} \xrightarrow{SOCl_2} \underset{(V)}{CH_3OCH{=}CClCOCl}$$

The acid chloride of the acetal of formylchloroacetic acid was not formed by this reaction, since cleavage of the alcohol apparently is the first step of the reaction. Usually cleavage of alcohols of a similar type from the acetals proceeds by the action of mixtures of bases (quinoline or pyridine) with the acid halides of the acids.

EXPERIMENTAL

The dimethylacetal of methyl formylacetate (I, R = CH_3). To sodium alcoholate, prepared from 34.5 g of sodium (1.5 g-at) and 48 g of anhydrous methanol in 500 ml of anhydrous ether, at −5° and with stirring, a mixture of 108 g (1.8 moles) of methyl formate and 133 g (1.8 moles) of ethyl acetate was added gradually. The reaction substance was stirred for 6 hours and left overnight at room temperature. The precipitate was filtered off, washed with anhydrous ether and dried. 63.8 g of the sodium derivative of the ester of formylacetic acid was obtained.

The sodium derivative (63.8 g) was added, with stirring, to 350 ml of anhydrous methanol, cooled to −5°, and containing 80 g of dry HCl.

The reaction substance was stirred for 12 hours at room temperature and neutralized with dry $NaHCO_3$. The precipitate was filtered off, and washed with anhydrous methanol. The methanol was removed in vacuo to $\frac{1}{4}$ of its original volume, and the residue was poured into ice water and extracted with ether. The ether extract was dried with magnesium sulfate. After removal of the ether, 20 g of the acetal with a b.p. of 73-74° at 17 mm was obtained. In the literature a b.p. of 77° at 22 mm was indicated for methyl β,β-dimethoxypropionate.

The dimethylacetal of formylacetic acid (II). With ice cooling, 55 ml of a methanol solution of KOH (2 moles) was added to 16.2 g (0.1 mole) of dimethylacetal of ethyl formylacetate in 20 ml of anhydrous methanol, and left for 20 hours at room temperature, after which half the KOH used was neutralized with an alcoholic solution of HCl; the potassium chloride which precipitated was filtered off. The filtrate was evaporated in vacuo, the residue was dissolved in 20 ml of water, acidified with 15% hydrochloric acid to an acid reaction to Congo, and repeatedly extracted with ether. The ether extract was dried with magnesium sulfate. The ether was removed in

vacuo, and 13 g (97%) of the dimethylacetal of formylacetic acid was obtained. The colorless, mobile liquid mixed with water in all proportions.

The acid chloride of the formylacetic acid dimethylacetal (III). To 6.5 g (0.048 mole) of formylacetic acid dimethylacetal previously dried in a desiccator over phosphorus pentoxide, 12 g (0.1 mole) of thionyl chloride was added gradually, cooling with ice water and shaking. The reaction substance was kept at 50° for 3 hours.

The thionyl chloride was removed in vacuo, and the residue was distilled. 4.5 g (61%) of the acid chloride of the dimethylacetal of formylacetic acid, with a b.p. of 65-67° at 12 mm; was obtained.

It was a colorless, mobile liquid with a characteristic pungent odor.

d_{20}^{20} 1.1828, n_D^{20} 1.4378, MR_D 33.70; calculated 33.218.

Found %: C 39.6; H 5.78; Cl 23.65. $C_5H_9O_3Cl$. Calculated %: C 39.34; H 5.9; Cl 23.28.

The methyl ester of the formylchloroacetic acid dimethylacetal. 125 g of the sodium derivative of methyl formylchloroacetate, obtained from 60 g of methyl formate, 108.5 g of methyl chloroacetate and 23 g of sodium, was added with stirring to 600 ml of methanol containing 170 g of dry HCl and cooled to −5°. It was stirred for 12 hours and treated as described above.

75 g (41%) of the acetal of methyl formylchloroacetate was obtained. The b.p. was 95-97° at 18 mm.

The dimethylacetal of formylchloroacetic acid. 18.2 g (0.1 mole) of the dimethylacetal of methyl formylchloroacetate was dissolved in 20 ml of anhydrous methanol, and on cooling, 55 ml of an alcoholic solution of potassium hydroxide (2 moles) was added. After 20 hours half of the potassium hydroxide used was neutralized with an alcoholic solution of hydrochloric acid; the potassium chloride which precipitated was filtered off, the filtrate was evaporated in vacuo, the residue was dissolved in 20 ml of water, acidified with 15% hydrochloric acid to an acid reaction to Congo and repeatedly extracted with ether. The ether extract was dried with magnesium sulfate. The ether was removed in vacuo. 15 g (89%) of the dimethylacetal of formylchloroacetic acid was obtained as a colorless, mobile liquid. The neutralization equivalent was 168.3. The calculated molecular weight was 168.5.

α-Chloro-β-methoxyacrylic acid (IV). 10 g (0.083 mole) of thionyl chloride was added gradually to 14 g (0.083 mole) of α-chloro-β,β-dimethoxypropionic acid. On completion of the addition of thionyl chloride, the reaction substance was kept at 40-50° for 3 hours. The thionyl chloride was removed in vacuo, then 1 g of the acid chloride of α-chloro-β-methoxyacrylic acid (b.p. 80-83° at 2 mm) was distilled.

The non-distilling crystalline residue was washed with dry heptane and filtered off. 5.4 g (48%) of α-chloro-β-methoxyacrylic acid, with a m.p. of 172-174° (with decompn.), was obtained from water.

Found %: C 35.18; H 3.85; CH_3O 23.4. $C_4H_5O_3Cl$. Calculated %: C 35.16; H 3.66; CH_3O 22.71.

The acid chloride of α-chloro-β-methoxyacrylic acid (V). A) 23.8 g (0.2 mole) of thionyl chloride, with ice cooling, e, was added gradually to 10 g (0.059 mole) of α-chloro-β,β-dimethoxypropionic acid. After addition of all the thionyl chloride to the reaction substance, it was heated for 3 hours on the water bath. The thionyl chloride was removed in vacuo, and the residue was fractionated. 6 g of the acid chloride of α-chloro-β-methoxyacrylic acid (b.p. 75-78° at 2 mm) was obtained.

It was slowly hydrolyzed by cold water with the formation of α-chloro-β-methoxyacrylic acid with a m.p. of 172-174°. A mixed test sample with the acid obtained earlier melted at 172-174°.

B) 5.9 g (0.05 mole) of thionyl chloride was added to 3.7 g (0.027 mole) of α-chloro-β-methoxyacrylic acid. The reaction substance was heated on the water bath for 3 hours, after which it was fractionated in vacuo. 3.5 g (83.5%) of the acid chloride of α-chloro-β-methoxyacrylic acid was obtained, and its b.p. was 75-78° at 2 mm, n_D^{20} 1.6727.

Found %: C 31.12; H 2.74. $C_4H_4O_2Cl_2$. Calculated %: C 30.98; H 2.58.

The amide of α-chloro-β-methoxyacrylic acid. 0.8 g of the acid chloride of α-chloro-β-methoxyacrylic acid was dissolved in 50 ml of anhydrous ether and saturated with gaseous ammonia. The precipitate which came down was filtered off (0.25 g ammonium chloride). The ether was removed in vacuo. The oil which remained crystallized on standing. The amide which was recrystallized twice from benzene melted at 77-79°.

Found %: N 10.33. $C_4H_6O_2NCl$. Calculated %: N 10.33.

SUMMARY

1. The acid chloride of β,β-dimethoxypropionic acid was obtained.

2. It was shown that by the action of thionyl chloride on the acetal of α-chloroformylacetic acid, the alcohol was cleaved with the formation of α-chloro-β-alkoxyacrylic acid.

3. The acid chloride of α-chloro-β-methoxyacrylic acid was obtained.

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* See Consultants Bureau Translation, page 861.

INVESTIGATIONS IN THE FIELD OF HETEROCYCLIC COMPOUNDS

III. SYNTHESIS OF 7,8-DIMETHOXYISOCOUMARIN-3-CARBOXYLIC ACID

S. I. Kanevskaya* and S. I. Malinina

Until now isocoumarin and its derivatives had been little investigated and had not gained wide practical utilization; apparently, this is explained by the absence of staisfactory methods of their synthesis and their still little availability. Meanwhile, these compounds are of definite interest, since some of their representatives have been observed in plants [2, 3]; isocoumarin and its derivatives can be easily converted to isoquinoline derivatives [4], among which are a large number of alkaloids with valuable therapeutic properties. It is of interest to note that the majority of these alkaloids are alkoxylated isoquinoline derivatives. In connection with this it seemed to be of interest to develop a synthesis of some of the alkoxylated derivatives of isocoumarin, from which the corresponding derivatives of the isoquinoline series have been easily obtained. The present work was devoted to the synthesis of 7,8-dimethoxyisocoumarin-3-carboxylic acid.

We encountered very few data in the literature on methods of synthesis of isocoumarincarboxylic acids. Here first and foremost belong the works of Bamberger and Kitschelt [5], and also Zincke [6], who obtained isocoumarin-3-carboxylic acid by oxidation of naphthoquinone with calcium hypochlorite. Isocoumarin-4-carboxylic acid was obtained by Dieckmann and Meiser [7] by the condensation of homophthalic ester with ethyl formate, and subsequent cyclization of the formyl derivative. A modification of this method was the synthesis of Vorozhtsov and Bogusevich [8], who instead of ethyl formate, introduced the diethyl ester of oxalic acid into the reaction, and obtained isocoumarin-3,4-dicarboxylic acid by cyclization, and obtained isocoumarin-3-carboxylic acid from it by means of partial decarboxylation. Unfortunately, because of lack of availability of the starting materials, all of these methods were found to be unsuitable for the synthesis of the isocoumarincarboxylic acids which were substituted in the benzene nucleus.

An interesting attempt made in this direction by a group of English authors [9] should be noted. Requiring 7,8-dimethoxyisocarbostyryl for their work, these investigators tried to obtain 7,8-dimethoxyisocoumarin-3-carboxylic acid, which after amination and subsequent decarboxylation should probably give 7,8-dimethoxyisocarbostyryl, by intramolecular closure of opianoylhydroxy acetate. However, these authors did not succeed in closing the isocoumarin ring in this way. Later this attempt was repeated by Schorigin and his coworkers [10]; whereupon they found that this closure proceeds with difficulty even under very rigid conditions, and the yield of isocoumarin-3-carboxylic acid amounted to hardly 8-10%.

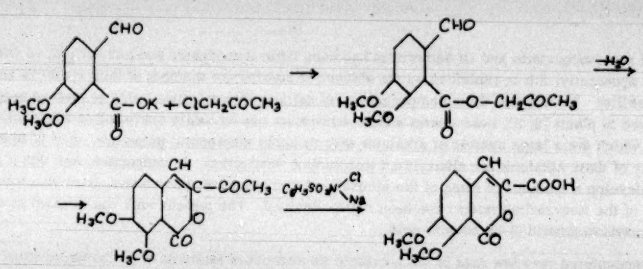
It was found by one of us in collaboration with Shemjakin [1] that opianoylhydroxyacetone, unlike opianoylhydroxy acetate undergoes intramolecular closure with ease, giving a highe yield of methyl-(7,8-dimethoxyisocoumaryl-3)-ketone; therefore, it seemed to us of interest to use this ketone for the synthesis of the acid. As is known, one of the most prevalent methods of conversion of similar type ketones to acids is their oxidation by hypochlorites [11]. However, in the use of this reaction in a given concrete case it is necessary to keep in mind that the isocoumarin series acids themselves, as found by Schmidt [12], are readily oxidized by the hypochlorites, being converted to acids of the benzene series; therefore, it is doubtful that we can expect high yields of the isocoumarincarboxylic acid. And actually, in the first attempt of oxidation of methyl-(7,8-dimethoxyisocoumaryl-3)-ketone with hypochlorite solutions we observed that the chief reaction product was a mixture of acids of the benzene series; even by adherence to very mild reaction conditions we were able to detect only traces of isocoumarincarboxylic acid.

In searches for a milder oxidizing agent we turned our attention to another source of active chlorine, namely, to chloramine. We carried out the reaction with the theoretical quantity of chloramine B by heating on the water bath in an aqueous medium; moreover, at the beginning of the heating we were able to detect the formation of chloroform; together with it a large quantity of benzamide was formed. Investigation of the reaction mixture after completion of the reaction showed that in this case we were also unable to avoid completely the severe oxidative processes: a large quantity of benzene series acids, not studied at present, were obtained just the same, together

* Deceased.

with the isocoumarincarboxylic acid. But the reaction definitely took place more smoothly, and the yield of 7,8-dimethoxyisocoumarin-3-carboxylic acid reached 38-50%, whereupon the acid was obtained at once in analytically pure form.

Thus, the synthesis of 7,8-dimethoxyisocoumarin-3-carboxylic acid may be carried out from available opianic acid according to the following scheme:



EXPERIMENTAL

2.48 g (0.01 mole) of methyl-(7,8-dimethoxyisocoumaryl-3-)-ketone, obtained by a method described earlier [1], was introduced into an aqueous solution of 7.8 g of chloramine B (0.03 mole) in 100 ml of water and heated on the water bath (bath temperature 75-80°), until complete dissolving of the ketone and cessation of formation of chloroform. The solution was cooled and filtered from the benzamide which crystallized.

The filtrate obtained was extracted with 50 ml of ether in order to remove the benzamide, and with vigorous stirring was acidified with hydrochloric acid (1:2) to an acid reaction to Congo. The slightly cream-colored crystals of 7,8-dimethoxyisocoumarin-3-carboxylic acid precipitated at once; the yield was 38%. The m.p. was 262°; after recrystallization from alcohol the m.p. was 264°, which corresponded to the literature value.

On titration with a hot solution of alkali the substance behaved as the lactonic acid, absorbing 2 equivalents of sodium hydroxide.

Found: equiv. 124.9. $C_{12}H_{10}O_5$. Calculated: equiv. 125.

By a 2-hour boiling with a solution of 25% ammonia the acid was converted quantitatively to the nitrogen-containing acid, which according to its melting point and analysis was identified as 7,8-dimethoxyisocarbostyryl-3-carboyxlic acid.

Found %: N 5.72. $C_{12}H_{11}O_5N$. Calculated %: N 5.62.

SUMMARY

It was found that methyl-(7,8-dimethoxyisocoumaryl-3)-ketone, obtained by intramolecular closure of opianoylhydroxyacetone, could serve as the starting material for the production of 7,8-dimethoxyisocoumarin-3-carboxylic acid. The latter was obtained in a yield of 38-50% by oxidation of the ketone with chloramine.

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SYNTHESIS OF ETHYLENIMINES

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Requiring some N-alkyl-substituted ethylenimines, we synthesized them by the Wenker method [1] by Cairns' modification [2], which consisted of the fact that an amino alcohol is slowly heated with sulfuric acid; the crude β-aminoalkylsulfuric acid obtained is heated with an alkali solution, and the imine which forms as an aqueous solution is distilled, and then is salted out with alkali. However, the yields of the N-isopropyl- and N-(2-butyl)-ethylenimines obtained in this way, amounted all told to about 40%. (See Table, Method A). Besides, it was observed that after distillation of the N-(2-butyl)-ethylenimine a rather large oily layer remained in the reaction solution, which was shown for the most part to be N-2-(butyl)-aminoethanol. Exactly the same picture was observed in work with N-(2-butyl)-aminoethylsulfuric acid, obtained by the action of chlorosulfonic acid on the amino alcohol hydrochloride [3]. Although the origin of the N-(2-butyl)-aminoethanol which we obtained would have been easier altogether to explain by the incompleteness of esterification of the amino alcohol, it was not excluded that at the time of heating the aminoalkylsulfuric acid with the alkali, together with the formation of the imine, hydrolysis of the ester proceeded partially, and that such a partial hydrolysis was one of the reasons for the reduction of the yields obtained by this method.

Other well-known modifications of the production of ethylenimines according to Wenker [3, 4], as indicated by their authors' descriptions, give much better results, but with the use of these modifications we have to distill large volumes of liquid and separate the imine from a dilute solution.

This induced us to develop the method that E. I. Vorobyeva and we proposed during the production of ethylenimine from β-chloroethylamine hydrochloride [5], which was a modification of the Gabriel reaction [6], and to extend it to the synthesis of the alkyl-substituted ethylenimines.

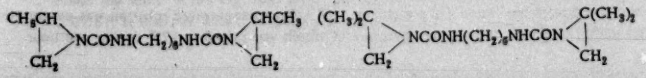
The β-chloroalkylamine hydrochlorides were formed by the action of thionyl chloride on the hydrochlorides of primary and secondary β-amino alcohols in a chloroform medium [7, 8, 9]. In order to remove the resinous impurities we heated an aqueous solution of the β-chloroalkylamine hydrochlorides with carbon and vacuum evaporated the filtrate to dryness. The β-chloroethylamine hydrochloride, obtained in a yield of 95-96% and in the absence of an inert solvent, after removal of the excess of thionyl chloride and volatile reaction products, could be used without additional purification for further work.

In order to convert it to the 1,2-alkylenimine, the β-chloroalkylamine hydrochloride was heated with an alkali solution, and the cyclic base which formed was separated as indicated above. The distillation should be made only after preliminary heating of the reaction mixture at 70-75° in the case of the C- and N-alkyl-substituted ethylenimines. In the initial experiments for production of 1,2-propylenimine, in which the distillation was carried out at once after mixture of the β-chloropropylamine hydrochloride with the alkali, at the time of the subsequent fractionation the greater part of the amine, separated from the distillate and dried, was invariably polymerized. Apparently, polymerization proceeded under the influence of the unsuccessful closing into a ring of β-chloropropylamine, entrained with vapors of 1,2-propylenimine.

As is evident from the data cited in the Table (see Table, Method B) high yields of the ethylenimines of the β-chloroalkylamines were obtained. The method was convenient, simple and we have used it successfully for a long time.

In passing, in the present work we described 1,6-hexamethylene-di-[N,N-(1'-methyl)-ethylene urea] (I) and 1,6-hexamethylene-di-[N,N-(1',1'-dimethyl)-ethylene urea] (II), which were obtained, respectively, by the reaction of 1,2-propylenimine and 2,2-dimethylethylenimine [2], with 1,6-hexamethylene diisocyanate, and were also synthesized from 2,2-dimethylethylenimine and the toluylenediisocyanate of toluylene-di-[N,N-(1',1'-dimethyl)]-ethylene urea (III).

E. N. Markacheva took part in the work.



(I) (II)

TABLE

Imine	Method of production	Yield (in %)	Boiling point (a)	Found (%)			Calculated (%)		
				C	H	N	C	H	N
Ethylenimine	B	63.7 (61 b)	55-57°						
1,2-Propylenimine	A	49-54 (c)	66-67						
	B	73.8[d] (59 b)							
N-Isopropylethylenimine	A	40-43							
	B	59 (52.7 b)	67-68	70.56	13.15	16.43	70.52	13.02	16.46
N-(2-butyl)-ethylenimine	A	35-40; 35.5[e]							
	B	71.7 (64.8 b)	96.5-98	72.81	13.50	13.84	72.65	13.22	14.13
N-(2-pentyl)-ethylenimine	A	33.39 e, f	121-124	74.10	13.48	12.40	74.26	13.36	12.38
N-cyclohexylethylenimine	B	58.4 (56.8 b)	60/25 mm	76.50	11.94	11.44	76.74	12.07	11.19

a) Distillation of the imines was made from a flask with a short, branched fractionating column. The constants of the imines, except N-(2-pentyl)-ethylenimine, cited in the Table, were purified by means of precise fractional distillation from a column, see [10].

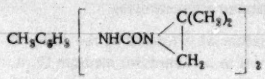
b) The yield of the imine on conversion to the corresponding amino alcohol is indicated in parentheses.

c) From isopropanolamine.

d) From β-chloropropylamine hydrochloride, obtained similarly to the β-chloroethylamine hydrochloride or the N-(2-butyl)-aminoethyl chloride hydrochloride

e) N-alkylaminoethylsulfuric acid was obtained by the action of chlorosulfonic acid on an amino alcohol hydrochloride.

f) d_4^{20} 0.7847.



(III)

EXPERIMENTAL

Ethylenimine. (According to E. I. Vorobyeva and V. A. Skorodumov's experiment). Into a three-necked flask, equipped with a stirrer with a mercury seal, a dropping funnel, a sturdy reflux condenser and a thermometer, we placed 135 g of aminoethanol hydrochloride, obtained by vacuum evaporation of its aqueous solution, and containing ca 5% of moisture, and added 130 ml of thionyl chloride dropwise at 5-10°. The mixture was heated slowly to 55°, stirred at this temperature for 1.5-2 hours until the liquifying reaction substance did not solidify, kept on a boiling bath for 45-60 minutes and then the excess of thionyl chloride, hydrogen chloride and sulfurous anhydride were carefully removed by heating in the vacuum of a water-jet pump. The yield of crude β-chloroethylamine hydrochloride was 150-152 g. The substance was very hygroscopic.

100 g of the crude β-chloroethylamine hydrochloride, with continuous stirring, was heated with 340 ml of a 27% solution of potassium hydroxide, and 100 ml of a liquid was distilled, which was collected in a vessel cooled with ice and salt. On cooling and stirring the distillate was saturated with ca. 100 g of potassium hydroxide; the ethylenimine layer which separated was dried with fused potassium hydroxide, preferably in a refrigerator, and distilled, collecting the 55-75° fraction. This fraction was dried with metallic sodium and distilled again. The ethylenimine yield was 23 g, and its b.p. was 55-57°.

We were able to separate an additional quantity of ethylenimine from the residue in the flask after distillation of the 55-75° fraction by addition of potassium hydroxide.

N-(2-butyl)-ethylenimine. Method A. a) 26.3 g of 93.1% sulfuric acid in 50 ml of water was added gradually, with cooling, to a solution of 31 g of N-(2-butyl)-aminoethanol [11] in 50 ml of water, and the water was driven off from the mixture until the temperature of the liquid did not rise to 115°. The concentrated solution was evaporated in the vacuum of a water jet pump, on an oil bath the temperature of which was raised to 175° during one hour.

maintained in vacuo at 175° (in the bath) for 2 hours and the still-warm residue, as far as possible, was crushed with a knife. Then 40 g of sodium hydroxide in 60 ml of water was poured into the solution and ca. 35 ml of the liquid was driven off. On cooling and stirring, 25 g of potassium hydroxide was added to the distillate, the N-(2-butyl)-ethylenimine which separated was dried overnight with fused potassium hydroxide, poured into a small flask with a branched fractionating column ca. 20 cm long, metallic sodium was added, it was left for several hours and distilled, collecting the 96-99° fraction. The yield was 10 g (38.1%). On a second distillation the b.p. was 96.5-98°.

After distillation of the N-(2-butyl)-ethylenimine, which contained a considerable oily layer, the residue of the reaction solution was filtered off from the mineral salt, the filtrate was extracted with benzene, and the benzene extracts were dried with potash and distilled; at this time 3.7 g by weight of the 85-100° (19 mm) fraction was collected, and 1.65 g by weight of the 100-160° (20 mm) fraction was collected. After a second distillation the first of these fractions had a b.p. of 89-90° (18 mm), n_D^{25} 1.4435, which corresponded to the constants of N-(2-butyl)-aminoethanol.

Found %: C 61.73; H 12.92; N 11.55. $C_6H_{15}ON$. Calculated %: C 61.48; H 12.90; N 11.96.

b) 16 g of N-(2-butyl)-aminoethanol was dissolved in 120 ml of dry ether, and with cooling by ice, dry hydrogen chloride was passed through until there was an increase in weight of 5.5-6 g. 13.5 ml of freshly-distilled chlorosulfonic acid was added gradually to the hydrochloride which was filtered off, and from which the ether was removed, heated for 40 minutes at ca. 90°; the excess of chlorosulfonic acid was removed by the vacuum of a water-jet pump; heating proceededfor 1.5 hours in vacuo at ca. 145° (in bath). On cooling with ice and salt, a solution of 28 g of sodium hydroxide in 42 ml of water was gradually added to the residue, and with stirring, on an oil bath, 16 ml of liquid was distilled, from which N-(2-butyl)-ethylenimine was separated as indicated in part a. The yield was 4.8 g (35.5%).

Method B. N-(2-butyl)-aminoethyl chloride was obtained similarly to other alkylaminoalkyl chlorides [9]: a solution of 58.5 g (0.5 mole) of N-(2-butyl)-aminoethanol in 375 ml of dry chloroform, which contained no alcohol, with stirring and at a temperature of 3-5° was saturated with hydrogen chloride; then on cooling 90 ml of thionyl chloride was added during 1.5 hours, and it was boiled for 1.5 hours. On the next day the chloroform and the excess of thionyl chloride were removed in vacuo, the residue was dissolved in 150 ml of water, boiled with carbon, filtered and vacuum evaporated to dryness. The N-(2-butyl)-aminoethyl chloride hydrochloride, after additional drying at 60-70°, had a m.p. of 130-141°. The yield was 80.2 g or 90.4% of the theoretical. The pure N-(2-butyl)-aminoethyl chloride hydrochloride melted at 138.5-140° (from anhydrous alcohol).

0.1798 g sub.: 0.2999 g AgCl. Found %: Cl 41.26. $C_6H_{15}NCl_2$. Calculated %: Cl 41.22.

71 g of the N-(2-butyl)-aminoethyl chloride hydrochloride (0.4 mole) was mixed with 160 ml of a 27% solution of potassium hydroxide, heated with stirring to ca. 75°, and maintained at this temperature for 45 minutes, after which, without stopping the stirring, distillation was begun, which was carried out at 82-104° (thermometer in the liquid). 75 ml of the distillate was collected, which was treated as indicated in the description of Method A. The yield of N-(2-butyl)-ethylenimine, with a b.p. of 96.5-99°, was 28.4 g (71.7%).

1,6-Hexamethylene-di-[N,N-(1'-methyl)-ethylene urea]

1.2 ml of 1,2-propylenimine in 7 ml of anhydrous ether was added gradually to a solution of 1.41 g of 1,6-hexamethylene diisocyanate in 7 ml of anhydrous ether cooled by ice water. Toward the end of the addition of the imine an oily residue separated, which soon solidified. After several days the residue was separated and washed with ether. The yield was 2.1 g and the m.p.was 58-61°. For purification, the substance was dissolved in a large quantity of boiling, anhydrous ether by the use of carbon, and the filtrate was evaporated to a small volume. The pure 1,6-hexamethylene-di-[N,N-(1'-methyl)-ethylene urea] melted at 64-66°. The substance was readily soluble in water, alcohol, benzene and chloroform.

3.827 mg sub.: 8.352 mg CO_2; 3.160 mg H_2O. 3.070 mg sub: 4.38 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: C 59.56; H 9.24; N 19.98. $C_{16}H_{32}O_2N_4$. Calculated %: C 59.53; H 9.28; N 19.85.

1,6-Hexamethylene-di-[N,N-(1',1'-dimethyl)-ethylene urea]

This compound was obtained by the action of 2,2-dimethylethylenimine on 1,6-hexamethylenediisocyanate similarly to the preceding compound. After recrystallization from anhydrous ethyl acetate (1:30), there were needles with a m.p. of 131-132°.

3.449 mg sub: 7.794 mg CO_2; 2.919 mg H_2O. 7.539 mg sub.: 9.64 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: C 61.67; H 9.47; N 17.91. $C_{16}H_{32}O_2N_4$. Calculated %: C 61.88; H 9.74; N 18.06.

The substance was soluble in water and in alcohol, difficultly soluble in ether and in petroleum ether, and could be recrystallized from actone.

Toluylene-di-[N,N-(1',1'-dimethyl)-ethylene urea]. Like the substance described above it was obtained by the action of 2,2-dimethylethylenimine on 1,2,4-toluylenediisocyanate, which contained an admixture of 1,2,6-toluylenediisocyanate. The yield was about 90%. After recrystallization from anhydrous ethyl acetate the m.p. was 155-158°.

3.675 mg sub.: 8.660 mg CO_2; 2.520 mg H_2O. 4.739 mg sub.: 5.90 ml 0.01 N H_2SO_4 (Kjeldahl). Found %: C 64.31; H 7.67; N 17.42. $C_{17}H_{24}O_2N_4$ Calculated %: C 64.52; H 7.65; N 17.72.

The substance was readily soluble in chloroform, moderately soluble in water, and difficultly soluble in ether and in carbon tetrachloride.

SUMMARY

1. The preparation of ethylenimine, 1,2-propylenimine, N-isopropyl-, N-(2-butyl)-, N-(2-pentyl)-, and N-cyclohexylethylenimine synthesized by Wenker's method as modified by Cairns, or from the hydrochlorides of the corresponding β-chloroalkylamines, either by that or by a different method was described.

2. The method of preparation of ethylenimines from the hydrochlorides of β-chloroalkylamines gave the best yields.

3. The corresponding substituted diureas were obtained by the reaction of 1,2-propylenimine with 1,6-hexamethylenediisocyanate and 2,2-dimethylethylenimine with 1,6-hexamethylenediisocyanate and toluylenediisocyanate.

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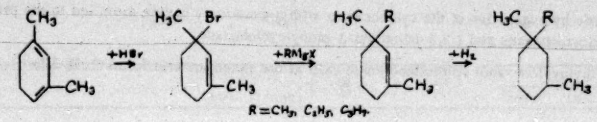
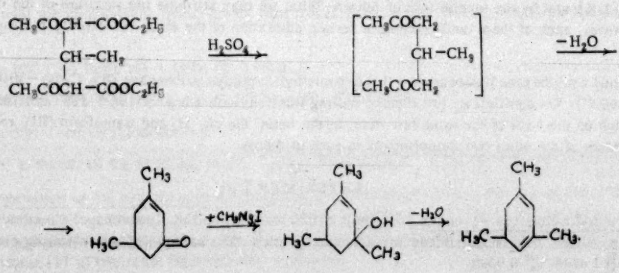
XLVII. SYNTHESIS OF CYCLOHEXENE AND CYCLOHEXANE HYDROCARBONS WITH A QUATERNARY CARBON ATOM ON THE BASIS OF 1,3,5-TRIMETHYLCYCLOHEXADIENE-1,3

Ya. Levina, Kim Dyai Gir and N. P. Shusherina

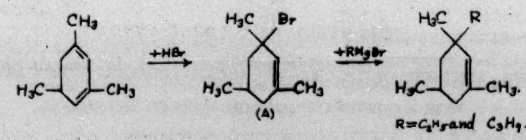
In our previous report [1] a new method of synthesis of the cyclohexene and cyclohexane hydrocarbons with a quaternary carbon atom, on the basis of 1,3-dimethylcyclohexadiene-1,3, was described. Dimethylcyclohexadiene was converted by hydrobromination to the tertiary allyl bromide, the reaction of which with organomagnesium compounds leads to the preparation of the 1,3-dimethyl-1-alkylcyclohexenes; the 1,3-dimethyl-1-alkylcyclohexanes were obtained by catalytic hydrogenation of the 1,3-dimethyl-1-alkylcyclohexenes:



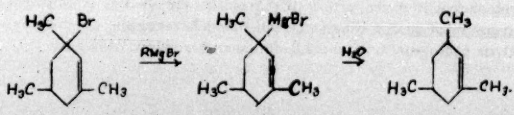
The structure of the cyclohexene hydrocarbons which were synthesized (presence of a quaternary carbon atom in them) was confirmed by their passive behavior toward the Zelinsky irreversible catalysis and also by investigation of the Raman spectra obtained from their trialkylcyclohexanes. This method of synthesis was used in the present work for the preparation of the 1,3,5-trimethyl-1-alkylcyclohexenes, and correspondingly, the 1,3,5-trimethyl-1-alkylcyclohexanes. 1,3,5-Trimethylcyclohexadiene-1,3 (dihydromesitylene), which was synthesized by the action of methylmagnesium iodide on 1,3-dimethylcyclohexene-1-one-3 (product of ketonic cleavage of ethylidene-bis-acetoacetic ester) served for a while as the initial cyclic diene hydrocarbon with a conjugated system of double bonds:



By the addition of one molecule of hydrogen bromide to 1,3,5-trimethylcyclohexadiene-1,3, the tertiary allyl bromide was obtained which, also like the dimethylcyclohexadiene hydrobromide described earlier [1], could not be investigated by the allylic rearrangement because of the peculiarity of its structure; by the reaction of this tertiary bromide (A) with organomagnesium compounds, cyclohexene hydrocarbons with a quaternary carbon atom — 1,3,5-trimethyl-1-ethylcyclohexene-2 and 1,3,5-trimethyl-1-propylcyclohexene-2, which were not described in the literature, were obtained:

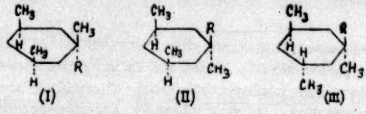


In each individual case, on distillation of the products of these reactions a hydrocarbon was separated, which, judging from its constants, was 1,3,5-trimethylcyclohexene-2. The formation of this hydrocarbon may be dependent on the replacement of a bromine atom in the original hydrobromide by the MgBr-group,* which occurs by side reactions:



The catalytic hydrogenation of the cyclohexenes with a quaternary carbon atom led to the production of 1,3,5-trimethyl-1-ethylcyclohexane and 1,3,5-trimethyl-1-propylcyclohexane.

The tetraalkylcyclohexanes synthesized could exist as the stereoisomeric forms (I, II, III):



Actually, 1,3,5-trimethyl-1-ethylcyclohexane (R = C_2H_5), unlike the corresponding cyclohexene hydrocarbon, distilled in a range of 2.5° (176.5-179°). By distillation we were able to separate two closely-boiling fractions (with b.p. of 176.5-176.7 and 178.5-179°), to which, according to the law established for the stereoisomeric 1,3-dimethylcyclohexanes [3, 4], and by the inverse rule of Auwers-Skita, we may attribute the structure of the cis- (I) and trans-form (III) (however, each of them could contain a certain admixture of the other two closely-boiling stereoisomeric forms).

The second cyclohexane hydrocarbon – 1,3,5-trimethyl-1-propylcyclohexane (R = C_3H_7) – distilled in a range of 4° (194.7-198.7°). On distillation, two closely-boiling fractions with a b.p. of 194.7-195° and 198.5-198.7° were separated, which on the basis of the same law were, in the main, the cis- (I) and trans-form (III), respectively, (with possible admixture of the other two stereoisomers to each of them).

EXPERIMENTAL

1,5-Dimethylcyclohexen-1-one-3 in a yield of 69% was obtained by Knoevenagel's method [5] – by the action of dilute sulfuric acid on ethylidene-bis-acetoacetic ester. The ketone had the following constants: b.p. 73° (6 mm), n_D^{20} 1.4348, d_4^{20} 0.9362.

1,3,5-Trimethylcyclohexadiene-1,3 (dihydromesitylene) was synthesized by the reaction of 1,5-dimethylcyclohexen-1-one-3 with methylmagnesium iodide by a method which we described earlier for the production of 2,4-dimethylpentadiene-1,3 [6]; on distillation from a column (with 40 theoretical plates) in a current of nitrogen over sodium, the hydrocarbon (77% yield) distilled in a wide temperature range (145-150° at 747 mm) and, apparently, it was a mixture of dihydromesitylene and its isomeric hydrocarbon with a heptacyclic double bond, which was formed by dehydration of the tertiary alcohol – 1,3,5-trimethylcyclohexen-1-ol-3.

* A similar reaction was described in one of our previous reports [2].

On repeated distillation of 50 g of the hydrocarbon (at 747 mm) the following fractions were separated: 1st, b.p. 145-146°, 4 g, n_D^{20} 1.4715; 2nd, b.p. 146-147°, 13 g, n_D^{20} 1.4740; 3rd, b.p. 147-149°, 13 g, n_D^{20} 1.4775; 4th, b.p. 149-150°, 18.3 g, n_D^{20} 1.4815.

Since the hydrocarbons with a heptacyclic double bond usually have higher constants than their isomeric hydrocarbons with double bonds in the ring, it can be assumed that dihydromesitylene was included chiefly in the low-boiling fractions. The second fraction had the following constants:

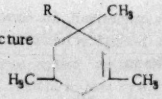
B.p. 146-147° (747 mm), n_D^{20} 1.4740, d_4^{20} 0.8279, MR_D 41.48. C_9H_{14}. Calculated: MR_D 40.63, EM_D 0.85.

Literature data: b.p. 61-66° at 38 mm; 150-152.5°, $n_D^{20.1}$ 1.48074, $d_4^{20.1}$ 0.8280 [7], b.p. 147°, d_4^{18} 0.8260 [8].

The addition of hydrogen bromide to dihydromesitylene (1,3,5-trimethylcyclohexadiene)* was carried out by cooling with snow and salt; a current of dry hydrogen bromide was passed into the hydrocarbon until attainment of a gain in weight corresponding to the addition of one molecule of hydrogen bromide (18 g). Immediately after preparation, the hydrobromide was dissolved in an equal volume of ether and reacted with organomagnesium compounds.

TABLE

Hydrocarbons of the General Structure



Name	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Yield (%)
1,3,5-Trimethyl-1-ethylcyclohexene-2	175° (744)	1.4525	0.8099	50.68	50.33	44
1,3,5-Trimethyl-1-propylcyclohexene-2	192 (745)	1.4563	0.8139	55.56	54.95	38

Reaction of the hydrobromide of 1,3,5-trimethylcyclohexadiene-1,3 with alkylmagnesium halides (RMgBr, where R = C_2H_5 and C_3H_7) was carried out under conditions which we described earlier for other tertiary allyl bromides [6, 9]. The reaction products of 1,3,5-trimethyl-1-alkylcyclohexene-2 were distilled over sodium from a column of 40 theoretical plates. The constants of the hydrocarbons (not described in the literature) and their yields are cited in the Table.

In both cases, on distillation of the reaction products, 1,3,5-trimethylcyclohexene-2 (17.7 and 17.6% yield) was separated with the cyclohexene hydrocarbons with a quaternary carbon atom (1,3,5-trimethyl-1-alkylcyclohexenes):

B.p. 140-142° (744 mm), n_D^{20} 1.4422, d_4^{20} 0.7955.

Literature data [10]: b.p. 142.5-143.5°, $n_D^{14.3}$ 1.4490, $d_4^{14.3}$ 0.8025.

For 1,3,5-trimethyl-1-ethylcyclohexene-2:

Found %: C 86.65, 86.62; H 13.40, 13.47. $C_{11}H_{20}$. Calculated %: C 86.84; H 13.16.

By hydrogenation of the cyclohexene hydrocarbons over platinized carbon (15% Pt), at 160-170°, the corresponding cyclohexane hydrocarbons, 1,3,5-trimethyl-1-ethylcyclohexane (b.p. 176.5-179° at 747 mm) and 1,3,5-trimethyl-1-propylcyclohexane (b.p. 194.7-198.7° at 749 mm), were obtained. On distillation of 1,3,5-trimethyl-1-ethylcyclohexane (17 g) two main fractions were separated:

1st, b.p. 176.5-176.7° (747 mm), 8.8 g, n_D^{20} 1.4410, d_4^{20} 0.7968, MR_D 51.13; calculated 50.80. Aniline point, 63.0°.

Found %: C 85.78, 85.63; H 14.49, 14.32. $C_{11}H_{22}$. Calculated %: C 85.71; H 14.29.

* Admixture of its isomeric hydrocarbon with a heptacyclic double bond to dihydromesitylene could not cause complication in the hydrobromination reaction, since the addition of hydrogen bromide to both isomeric hydrocarbons should lead to the formation of the same allylic type tertiary bromide (A).

2nd, b.p. 178.5-179° (747 mm), 3 g, n_D^{20} 1.4443, d_4^{20} 0.8035, MR_D 51.03; calculated 50.80. Aniline point, 60.6°.

Found %: C 85.85, 85.72; H 14.34, 14.40. $C_{11}H_{22}$. Calculated %: C 85.71; H 14.29.

On distillation of 1,3,5-trimethyl-1-propylcyclohexane (28 g) two main fractions were separated, which consisted of the stereoisomeric forms of 1,3,5-trimethyl-1-propylcyclohexane, and had the following constants:

1st, b.p. 194.7-195° (749 mm), 7.4 g, n_D^{20} 1.4441, d_4^{20} 0.7994, MR_D 55.92; calculated 55.41. Aniline point, 66.8°.

2nd, b.p. 198.5-198.7° (749 mm), 7.5 g, n_D^{20} 1.4472, d_4^{20} 0.8087, MR_D 55.60; calculated 55.41. Aniline point, 65.1°.

Found %: C 85.56, 85.46; H 14.63, 14.52. $C_{12}H_{24}$. Calculated %: 85.12; H 14.88.

SUMMARY

1. The method of synthesis of cyclohexene hydrocarbons with a quaternary carbon atom, which we developed earlier, was used for the production of 1,3,5-trimethyl-1-ethylcyclohexene-2 and 1,3.5-trimethyl-1-propylcyclohexene-2. The synthesis of these hydrocarbons was carried out by the reaction of organomagnesium compounds with the hydrobromide of 1,3,5-trimethylcyclohexadiene-1,3, which has an allylic type tertiary bromide.

2. By hydrogenation of the cyclohexene hydrocarbons synthesized, the corresponding cyclohexane hydrocarbons with a quaternary carbon atom in the ring — 1,3,5-trimethyl-1-ethylcyclohexane and 1,3,5-trimethyl-1-propylcyclohexane — were obtained as a mixture of the stereoisomeric forms.

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REACTION OF PHOSPHORUS PENTACHLORIDE WITH THE ESTERS OF OXAMIC ACID

TRICHLOROPHOSPHAZO-DICHLOROALKOXYACETYLS

A. V. Kirsanov and V. P. Molosnova

In 1877 O. Wallach [1] studied the reaction of phosphorus pentachloride with the ethyl ester of oxamic acid (oxamethane).

O. Wallach found that the reaction proceeded very readily and that one molecule of oxamethane reacted with one molecule of phosphorus pentachloride, but he isolated neither of the direct reaction products in the pure state. O. Wallach assumed, on the basis of analysis of the crude reaction products, that the process proceeds according to the scheme:

$$C_2H_5OCOCONH_2 + PCl_5 \longrightarrow POCl_3 + C_2H_5OCOCl_2NH_2.$$

i.e., with the formation of the corresponding "amide chloride." The chlorine content in O. Wallach's "amide chloride" differed from the calculated content at best by 4.12%. No reactions strictly demonstrating the structure of the substance as an amide chloride were carried out. By the action of the moisture of the air on the crude reaction product, O. Wallach obtained a substance of the composition $C_4H_6O_3Cl_4NP$ in the pure state. In O. Wallach's opinion, this substance formed from the amide chloride and phosphorus oxychloride under the influence of the moisture of the air which, of course, was not very likely. By the action of alcohols and phenols on the crude "amide chloride," O. Wallach [2] obtained ethyl chloride and the ester of oxamic acid with that alcohol or phenol which was taken for the reaction, i.e., the process should proceed according to the scheme:

$$C_2H_5OCOCCl_2NH_2 + ROH \longrightarrow C_2H_5Cl + HCl + ROCOCONH_2.$$

O. Wallach did not give the slightest plausible explanation for this strange course of the reaction. O. Wallach even assumed as demonstrated that, on the action of phosphorus pentachloride on the oxamethane, the primary reaction product was the corresponding amide chloride, and this statement was accepted without any criticism and until the present time was assumed to be correct.

The problem concerning the direction and mechanism of the reaction of phosphorus chloride with oxamethane and other esters of oxamic acid was of theoretical interest, since precisely this reaction was the only experimental basis of the assumption at the present time of the scheme of reaction of phosphorus pentachloride with unsubstituted amides of carboxylic acids. According to this scheme the amide chlorides were the primary reaction product, which decomposed at first into hydrogen chloride and imide chlorides, and then into hydrogen chloride and nitriles:

$$RCONH_2 + PCl_5 \longrightarrow RCCl_2NH_2 + POCl_3$$

$$RCCl_2NH_2 \longrightarrow RCCl{=}NH + RCN.$$

It was found in the experiment of the study of the reaction of phosphorus pentachloride with oxamethane that the reaction proceeds readily at room temperature and is completed very rapidly by heating at 30-40°; moreover, the reaction proceeds in two stages: the oxamethane can react with either one or two molecules of phosphorus pentachloride, which O. Wallach did not observe.

The reaction proceeds according to the scheme:

$$C_2H_5OCOCONH_2 + PCl_5 \longrightarrow POCl_3 + C_2H_5OCCl_2CONH_2$$

$$C_2H_5OCCl_2CONH_2 + PCl_5 \longrightarrow 2HCl + C_2H_5OCCl_2CON{=}PCl_3,$$

i.e., at first with the formation of the amide of dichloroethoxyacetic acid, and then of trichlorophosphazo-dichloroethoxyacetyl.

This scheme is entirely strictly demonstrated by the practically quantitative yields of the end reaction products (hydrogen chloride, phosphorus oxychloride and trichlorophosphazo-dichloroethoxyacetyl), and also by the elementary composition, molecular weight and chemical properties of the intermediate and end products of the reaction (the amide of dichloroethoxyacetic acid and trichlorophosphazo-dichloroethoxyacetyl.

According to the elementary composition and molecular weight of the intermediate reaction product the structure can be either the amide of dichloroethoxyacetic acid (I) or the amide chloride of oxamethane (II):

$C_2H_5OCCl_2CONH_2$ (I) $\qquad$ $C_2H_5OCOCCl_2NH_2$. (II)

The structure of the amide chloride (II) was completely eliminated, since the substance melted without decomposition, was stored at room temperature for months without decomposition, distilled at high vacuum without decomposition, was readily soluble in nonpolar solvents and had a low melting point (82°). The amide chloride could not have such chemical and physical properties, but these properties were extremely close to those of the esters of dichloroalkoxyacetic acids, which were formed readily by the action of phosphorus pentachloride on the ester of oxalic acid [3], according to the scheme:

$$C_2H_5OCOCOOC_2H_5 + PCl_5 \longrightarrow POCl_3 + C_2H_5OCCl_2COOC_2H_5.$$

According to the elementary composition and molecular weight the end product can have the structure of trichlorophosphazo-dichloroethoxyacetyl (III) or 1,1-dichloride-2-ethoxy-trichlorophosphazo-oxalyl (IV):

$C_2H_5OOCCl_2CON{=}PCl_3$ (III) $\qquad$ $C_2H_5OCOCCl_2N{=}PCl_3$. (IV)

Structure (IV) was discarded completely since phosphorus pentachloride should cleave a similar substance very readily with the formation of cyanocarbonic ester, which did not occur, and is not likely to form quantitatively from the amide of dichloroethoxyacetic acid (I). Moreover, not one case is known in which the amide of any monobasic carboxylic acid reacted with two molecules of phosphorus pentachloride.

It was found recently that trichlorophosphazosulfon compounds [4], by the action of the moisture of the air or of one equivalent of formic acid, readily give the acid dichlorides of the corresponding sulfonamidophosphoric acids. Therefore, it was natural to assume that the substance of the O. Wallach composition $C_4H_6O_3Cl_4NP$ was obtained by a similar method, as a result of partial hydrolysis of trichlorophosphazo-dichloroethoxyacetyl, according to the scheme:

$$C_2H_5OCCl_2CON{=}PCl_3 + H_2O \longrightarrow C_2H_5OCCl_2CONHPOCl_2.$$

A specially conducted experiment confirmed this assumption. By the action of one equivalent of formic acid on trichlorophosphazo-dichloroethoxyacetyl, the acid dichloride of dichlorethoxyacetylamidophosphoric acid was obtained almost quantitatively according to the scheme:

$$C_2H_5OCCl_2CON{=}PCl_3 + HCOOH \longrightarrow C_2H_5OCCl_2CONHPOCl_2 + CO + HCl.$$

This substance, of composition $C_4H_6O_3Cl_4NP$, was shown to be the same product separated by O. Wallach from the reaction mixture, after action of the moisture of the air on it. Consequently, O. Wallach's assumption of the fact that this substance formed from the amide chloride and phosphorus oxychloride is completely refuted.

O. Wallach's "amide chloride" reaction with alcohols and phenols (see above) was also easily accounted for. The amide of dichloroethoxyacetic acid, which occurs in the crude reaction products, reacted with alcohols or phenols, according to the scheme:

$$NH_2COCCl_2OC_2H_5 + ROH \longrightarrow NH_2COC(OC_2H_5)(OR)(Cl) \longrightarrow C_2H_5Cl + NH_2COCOOR \text{ or } RCl + NH_2COCOOC_2H_5.$$

i.e., with the formation of the initial oxamethane and the ester of oxamic acid with the alcohol which was used in the reaction.

It seems strange that O. Wallach was unable to separate the products which formed almost quantitatively. This is explained by three reasons. First, O. Wallach was completely confident that the reaction of phosphorus pentachloride with amides of the carboxylic acids proceeds only with the formation of "amide chlorides", and he neither assumed nor considered any other possible direction of the reaction, dogmatically limiting his concept and work to this premise. Second, O. Wallach did not observe that the reaction proceeds not only with one but also with two molecules of phosphorus pentachloride. Third, O. Wallach stored all of his substances in desiccators with soda lime or calcium chloride, which is completely inadmissible, since during such storage the phosphazo compounds are rapidly hydrolyzed, taking water away from the calcium chloride or soda lime.

The reaction of phosphorus pentachloride with the esters of oxamic acid was carefully studied in the instance of the ethyl ester of oxamic acid (oxamethane). Study of the reaction in several other instances showed that it has an entirely general character, and that by means of this reaction, the various trichlorophosphazo-dichloroalkoxyacetyls can be obtained almost quantitatively, and the amides of the dichloroalkoxyacetic acids can be obtained in high yields.

All these substances are low-melting, and some are liquids at room temperature. Their most characteristic chemical property is their high reactivity. Thus, for example, they react readily with water, alcohols, phenols, amines and organometallic compounds, and at the same time give various derivatives of phosphoric, oxalic and acetic acids.

EXPERIMENTAL

Reaction of Phosphorus Pentachloride with Oxamethane

A. Production of trichlorophosphazo-dichloroethoxyacetyl. 0.2 mole of pure, dry, pulverized oxamethane (23.4 g) and 0.4 mole + an excess of 1.0 g of pure, pulverized phosphorus pentachloride (84.4 g) were introduced into a 0.5-liter, round-bottomed flask, and the mixture was stirred vigorously by hand. The flask was closed immediately, with a reflux condenser in section and the upper end of the condenser was subsequently connected to a small bubble counter filled with concentrated sulfuric acid, and to a trap for hydrogen chloride with 200 ml of water. A rather vigorous reaction began immediately, which was accompanied by extensive cooling of the reaction mixture. The contents of the flask were completely liquified after 3 minutes. After 15 minutes, when the evolution of hydrogen chloride was observed to decrease, the flask was submerged in a water bath heated to 30° and during a period of 25 minutes the temperature was increased to 70°, (frequent stirring of contents of the flask by hand.) Hydrogen chloride was displaced from the flask and condenser by dry air, the apparatus was dismantled and the reaction flask was weighed. The weight of the mixture of phosphorus oxychloride and the crude trichlorophosphazo-dichloroethoxyacetyl was 93.0 g which, considering the excess of phosphorus pentachloride, amounted to 99.7% of the theoretical quantity. The hydrogen chloride yield was 0.384 equivalent (96.0%).

The phosphorus oxychloride was vacuum distilled at 5 mm, on a water bath heated to 70°, with the vessel cooled to −75°. The phosphorus oxychloride yield was 28.85 g (94.0%). Some phosphorus pentachloride was deposited in the condenser tube, the quantity of which was not determined. The residue in the flask was a colorless, slightly turbid liquid, which soon crystallized completely, warming strongly. The yield of crude trichlorophosphazo-dichloroethoxyacetyl was 62.5 g (101.7%), and the m.p. was 60-64° (thermometer bulb in the liquid).

After recrystallization from 125 ml of petroleum ether (b.p. 85-95°) trichlorophosphazo-dichloroethoxyacetyl was obtained as clear, colorless, coarse prisms with a m.p. of 71-72°. The yield was 53.0 g (86.2%). By concentration of the mother liquor 6.0 g more (9.7%) of a substance with a m.p. of 68-71° could be separated. Thus, the total yield of recrystallized product was 95.9%. In the preparation, and especially during the recrystallization, of the trichlorophosphazo-dichloroethoxyacetyl, it was necessary to protect the reaction mixture and the solutions from the action of the moisture of the air.

The trichlorophosphazo-dichloroethoxyacetyl was a colorless, crystalline substance, which was readily soluble in benzene, toluene, dioxan, dichloroethane and boiling petroleum ether, but was difficultly soluble in cold petroleum ether.

Found %: C 15.40, 15.47; H 1.59, 1.54; Cl 57.23, 57.57; N 4.45, 4.37; P 9.99, 9.91. M 289.0, 292.0. Equiv. after hydrolysis 7.98, 7.95 (thymolphthalein); 6.03, 6.01 (methyl orange). $C_4H_2O_2Cl_5NP$. Calculated %: C 15.63; H 1.64; Cl 57.68; N 4.56; P 10.08, M 307.36. Equiv. after hydrolysis 8.00 (thymolphthalein); 6.00 (methyl orange).

The trichlorophosphazo-dichloroethoxyacetyl was hydrolyzed readily by water, changed slowly on storage in the air, and reacted vigorously with alcohols, ammonia, amines, phenols and other substances which contained active hydrogen atoms.

B. Preparation of the amide of dichloroethoxyacetic acid. 0.2 mole (23.4 g) of pulverized oxamethane was added to a mixture of 0.2 mole (41.6 g) of pulverized phosphorus pentachloride and 50 ml of dry carbon tetrachloride, with continuous, vigorous stirring at room temperature. The reaction mixture gradually liquified, and almost no hydrogen chloride was evolved. If stirring ceased the evolution of gas was immediately accelerated, and the yields decreased. The process was completed after 20 minutes. The reaction mixture was a turbid, colorless liquid. Carbon tetrachloride and phosphorus oxychloride were vacuum distilled at 5 mm, on a water bath heated to 70°. The residue was a turbid liquid (36.9 g, 107%), which on cooling partially crystallized. In order to purify it, the crude product was recrystallized from 50 ml of carbon tetrachloride. The yield was 15.7 g (45.6%). By concentration several grams more of the product could be separated from the mother liquor. It was necessary to carry out all operations with protection of the reaction mixture and solutions from the moisture of the air.

The amide of dichloroethoxyacetic acid consisted of fine, colorless, lustrous needles with a m.p. of 81-82°. The substance was readily soluble in benzene, dioxan and acetone, but difficultly soluble in carbon tetrachloride and in petroleum ether. It reacted slowly with water in the cold, but rapidly on heating. It reacted readily with alcohols, alcoholates, amines, ammonia and other substances which contained active hydrogen atoms. Stored in the absence of moisture for months, it did not decompose.

Found %: C 27.85, 27.90; H 4.05, 4.07; Cl 41.12, 41.08; N 8.07, 8.12. M 160.0, 155.8. Equiv. after hydrolysis 2.94, 2.92 (phenolphthalein); 1.93, 1.95 (methyl orange). $C_4H_7O_3Cl_2N$. Calculated %: C 27.94; H 4.10; Cl 41.23; N 8.15. M 172.03. Equiv. after hydrolysis 3.00 (phenolphthalein); 2.00 (methyl orange).

Partial Acidolysis of Trichlorophosphazo-dichloroethoxyacetyl

Production of the acid dichloride of dichloroethoxyacetylamidophosphoric acid. 0.02 mole of trichlorophosphazo-dichloroethoxyacetyl (6.15 g) was dissolved in 10.0 ml of benzene, and 0.02 mole of anhydrous formic acid (0.92 g) was added. A very vigorous reaction began immediately with the formation of carbon monoxide and hydrogen chloride, and the mixture warmed up. After 5 minutes clear, colorless, coarse prisms began to precipitate. After several hours the crystals were filtered off by suction, washed with benzene and dried in the air, and the yield was 5.1 g. This substance was a crystalline compound of the acid dichloride of dichloroethoxyacetylamidophosphoric acid with a half molecule of benzene, and it completely lost the benzene on drying for 3 hours at 20° in vacuo at 2 mm.

Found %: C_6H_6 11.75. $C_4H_9O_3Cl_4NP \cdot 0.5C_6H_6$. Calculated %: C_6H_6 11.91.

1.25 g of a somewhat less pure product remained after evaporation of the benzene mother liquor in the air. Thus, the total yield of the crystallization compound with benzene was 6.35 g (96.0%).

The acid dichloride of dichloroethoxyacetylamidophosphoric acid crystallized from petroleum ether as red needles, with lengths of about 20 mm, and with a m.p. of 124-126° (agglomeration 120°). The substance was rather stable toward the moisture of the air, it was hydrolyzed slowly by cold water, rapidly by hot, and reacted readily with ammonia, amines and alcohols.

Found %: Cl 49.50, 49.29. Equiv. after hydrolysis 7.01, 7.05 (phenolphthalein); 5.10, 5.19 (methyl orange). $C_4H_8O_3Cl_4NP$. Calculated %: Cl 49.11. Equiv. after hydrolysis 7.00 (phenolphthalein); 5.00 (methyl orange).

General Method of Preparation of Trichlorophosphazo-Dichloroalkoxyacetyls

0.1 mole of pulverized, dry ester of oxamic acid was mixed with 0.2 mole of pulverized phosphorus pentachloride in a round-bottomed flask, closed with a reflux air condenser, which was protected by a Tishchenko bottle containing sulfuric acid. A reaction began after 2-3 minutes, the mixture liquified (absorption of heat) after 7-10 minutes, and the rate of liberation of hydrogen chloride diminished. The flask was submerged in a water bath heated to 30-40°. The reaction was practically complete after 20-30 minutes. The reflux condenser was replaced by a straight condenser, connected to a vacuum and to a vessel which was cooled to −20°. The phosphorus oxychloride was distilled at 5 mm and 50-60°. The crude trichlorophosphazo-dichloroalkoxyacetyl was in the residue. Thus, the following substances were obtained.

Trichlorophosphazo-dichloromethoxyacetyl, $CH_3OCCl_2CON{=}PCl_3$. The yield of the crude product was 100.0-103.0%; after recrystallization from petroleum ether it consisted of colorless, flat needles with a length of several millimeters, and a m.p. of 55-57°. The yield was about 90%.

Found %: Cl 59.99, 59.95. Equiv. after hydrolysis 6.01, 6.02 (methyl orange); 7.97, 7.95 (phenolphthalein). $C_3H_3O_2Cl_5NP$. Calculated %: Cl 60.45. Equiv. after hydrolysis 6.00 (methyl orange); 8.00 (phenolphthalein).

Trichlorophosphazo-dichloro-n-butoxyacetyl n-$C_4H_9OCCl_2CON{=}PCl_2$. The yield of the crude product was 101-102%, with a m.p. of −3+1° (thermometer bulb in the liquid). The crude product was analyzed.

Found %: Cl 53.21, 53.04, Equiv. after hydrolysis 8.17, 8.16, 8.18 (phenolphthalein). $C_6H_9O_2Cl_5NP$. Calculated %: C 52.88. Equiv. after hydrolysis 8.00 (phenolphthalein).

We were unable to recrystallize the trichlorophosphazo-dichlorobutoxyacetyl; therefore, in order to identify it, it was converted to the crystalline acid dichloride of dichlorobutoxyacetylamidophosphoric acid, by the action of formic acid in a benzene solution, followed by crystallization from petroleum ether. The yield of crude product was 70%, but recrystallized it was 60%. The acid dichloride of dichlorobutoxyacetylamidophosphoric acid n-$C_4H_9OCCl_2CONHPOCl_2$ consisted of fine, colorless needles with a m.p. of 114-116°.

Found %: Cl 44.33, 44.42, Equiv. after hydrolysis 6.98, 7.02 (phenolphthalein). $C_6H_{10}O_2Cl_4NP$. Calculated %: Cl 44.76. Equiv. after hydrolysis 7.00 (phenolphthalein).

Trichlorophosphazo-dichloroisobutoxyacetyl iso-$C_4H_9OCCl_2CON{=}PCl_2$. The yield of crude product was 102% with a m.p. of 28-31° (thermometer bulb in liquid); after recrystallization from petroleum ether it consisted of fine, colorless prisms.

Found %: Cl 53.18, 53.19. Equiv. after hydrolysis 8.05, 8.06 (phenolphthalein). $C_6H_9O_2Cl_5NP$. Calculated %: C 52.88. Equiv. after hydrolysis 8.00 (phenolphthalein).

Trichlorophosphazo-dichlorocyclohexoxyacetyl $C_8H_{11}OCCl_2CON{=}PCl_2$. The yield of crude product was 99.5%. The liquid, which did not crystallize at −20°, was very readily decomposed on heating or by partial hydrolysis, with the formation of cyclohexene and chlorocyclohexane. The crude product was analyzed.

Found %: Cl 48.16, 48.00; P 8.53, 9.25. Equiv. after hydrolysis 7.98, 8.02 (phenolphthalein). $C_8H_{11}O_2Cl_5NP$. Calculated %: Cl 49.07; P 8.58. Equiv. after hydrolysis 8.00.

All the trichlorophosphazo-dichloroalkoxyacetyls were readily soluble in benzene, toluene, dioxan and dichloroethane. The methoxy derivative was difficultly soluble in carbon tetrachloride and in petroleum ether. The solubility in carbon tetrachloride and in petroleum ether increased with enlargement of the alkoxy radical. The isobutoxy derivative was readily soluble in carbon tetrachloride, and rather readily soluble in petroleum ether.

SUMMARY

1. It was shown that the sole experimental basis of the O. Wallach scheme, present in the literature for the reaction of phosphorus pentachloride with the amides of carboxylic acids, was incorrect.

2. It was shown that, by the action of phosphorus pentachloride on oxamethane and other esters of oxamic acid, the reaction did not proceed with the formation of amide chlorides according to O. Wallach's scheme. In reality amides of dichloroalkoxyacetic acids and trichlorophosphazo-dichloroalkoxyacetyls were obtained.

3. A general method was developed for production of the trichlorophosphazo-dichloroalkoxyacetyls. Five trichlorophosphazo-dichloroalkoxyacetyls and the amide of dichloroethoxyacetic acid were synthesized and described.

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NEW METHOD OF SYNTHESIS OF THE ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS

XIX. ADDITION OF DIALKYLTHIOPHOSPHOROUS ACIDS AND ESTERS OF PHOSPHINOUS ACID TO UNSATURATED NITRILES AND VINYLPHOSPHINIC ESTER

A. N. Pudovik and N. G. Poloznova

In a series of previous reports we showed that, in the presence of alkali catalysts, the dialkylphosphorous acids add with extraordinary ease to acrylonitrile and to different unsaturated nitriles [1]. In the present work we studied the addition to acrylonitrile and to different types of partial esters of the phosphorus acids: the dialkylthiophosphorous acids and the esters of alkyl- and arylphosphinous acids. The addition of the dialkylthiophosphorous acids and the esters of phosphinous acids to acrylonitrile was carried out in the presence of alkali metal alcoholates. In order to prevent an exchange of radicals between the dialkylthiophosphorous acids and the partial esters of phosphinous acid, on the one hand, and the alcoholates, on the other, which takes place extensively during the reaction, both reagents were obtained with the same radicals.

We carried out the addition of dimethylthiophosphorous, diethylthiophosphorous, n-dibutylthiophosphorous, and diisobutylthiophosphorous acids, the ethyl and butyl esters of ethylphosphinous acid, and the ethyl ester of phenylphosphinous acid to acrylonitrile. The course of the addition reaction of the dialkylthiophosphorous acids to acrylonitrile can be represented by the following general scheme:

$$(RO)_2PSH + RONa \rightleftharpoons (RO)_2PSNa + ROH.$$

$$CH_2{=}CH{-}CN + (RO)_2PSNa \longrightarrow (RO)_2P(S)CH_2CHNaCN \quad \text{or}$$

$$(RO)_2P(S)CH_2CH{=}C{=}NNa \xrightarrow{(RO)_2PSH} (RO)_2P(S)CH_2CH_2CN + (RO)_2PSNa,$$

where R = CH_3, C_2H_5, n-C_4H_9, iso-C_4H_9.

The addition reactions of the partial esters of phosphinous acids are represented by analogous schemes. The addition products are colorless, viscous liquids with a disagreeable odor, insoluble in water, but highly soluble in organic solvents – alcohol, ether, benzene, and toluene. The properties of the products obtained are given in Table 1.

Using the above-described method of carrying out the reaction, we brought about the addition of the dialkylthiophosphorous acids and the partial esters of phosphinous acids to metacrylonitrile and vinylacetonitrile. In the former case the reaction proceeds according to the equation

$$(RO)_2PSH + CH_2{=}C(CH_3){-}CN \longrightarrow (RO)_2P(S)CH_2CH(CH_3)CN,$$

with the formation of the nitriles of β-(dialkylthiophosphon)-isobutyric acid, or in the case of the esters of ethylphosphinous acid, with the formation of the esters of β-(cyanopropyl)-ethylphosphinic acid.

The addition of the dialkylthiophosphorous acids and the esters of phosphinous acids to vinylacetonitrile proceeds analogously to the addition reaction of the dialkylphosphorous acids to allyl cyanide and crotononitrile [2].

$$CH_2{=}CHCH_2CN \overset{OR^-}{\rightleftharpoons} CH_3CH{=}CHCN \xrightarrow{(RO)_2PSH} (RO)_2P(S)CH(CH_3)CH_2CN$$

$$CH_3CH{=}CHCN \longrightarrow RO(R)P(O)CH(CH_3)CH_2CN \quad (R = OH)$$

TABLE 1

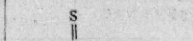
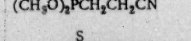
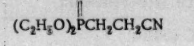
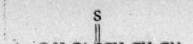
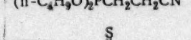
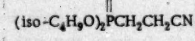
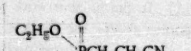
Test No.	Formula	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	Molec. refraction found	Molec. refraction calculated	Phosphorus content (%) found	Phosphorus content (%) calculated	Yield (%)
1		138-139° (14)	1.4860	1.1855	43.39	43.46	17.13, 17.44	17.36	59
2		134-135 (7)	1.4772	1.1095	52.79	52.70	15.15, 15.22	15.00	74
3		167 (5)	1.4741	1.0366	71.40	71.17	12.04, 12.05	11.8	68
4		174 (14)	1.4721	1.0245	71.39	71.17	11.90, 11.65	11.79	67
5		171-171.5 (12)	1.4527	1.0794	43.84	43.57	17.34, 17.24	17.72	67
6		192 (13)	1.4521	1.0291	52.55	52.80	14.87	14.95	53
7		162-163 (1)	1.5245	1.1478	59.49	59.79	14.06, 14.09	13.90	48

TABLE 2

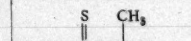
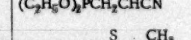
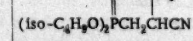
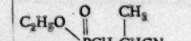
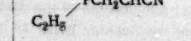
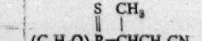
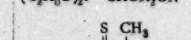
Test No.	Formula	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	Molec. refraction found	Molec. refraction calculated	Phosphorus content (%) found	Phosphorus content (%) calc'd.	Yield (%)
1		145-146° (10)	1.4730	1.0806	57.54	57.32	14.24, 14.31	14.03	56
2		189-189.5 (25)	1.4678	1.0075	75.77	75.79	11.59, 11.54	11.79	59
3		183-185 (17)	1.4470	1.0048	57.42	57.42	14.68, 14.70	14.29	40
4		124-125 (3)	1.4750	1.0840	57.46	57.32	13.89, 14.01	14.02	75
5		176-177 (10)	1.4698	1.0208	75.78	75.79	11.11, 11.09	11.18	62
6		178-178.5 (14)	1.4668	1.0134	75.91	75.79	10.96	11.11	75
7		158-159.5 (7)	1.4550	1.0597	48.43	48.19	16.29, 16.11	16.39	68

TABLE 3

Test No.	Formula	B.p. under pressure (mm)	n_D^{20}	d_4^{20}	Molec. refraction found	Molec. refraction calculated	Phosphorus and sulfur content (%) found	Phosphorus and sulfur content (%) calc'd	Yield (%)
1	$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$	163° (13)	1.4633	1.1356	77.49	77.60	P 19.26, S 9.68	P 19.49, S 10.06	66
2	$(n\text{-}C_4H_9O)_2\overset{S}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$	209 (5)	1.4510	1.0573	95.35	96.08	P 16.38	P 16.58	67
3	$C_2H_5O\diagdown\overset{O}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$ $C_2H_5\diagup$	195 (4)	1.4510	1.1235	68.60	68.47	P 21.37, 21.50	P 21.67	59

Reactions with metacrylonitrile and vinylacetonitrile took place less vigorously than with acrylonitrile. A short induction period was observed. The addition products are colorless, not very mobile liquids with a disagreeable odor, insoluble in water, but soluble in alcohol, ether, benzene and toluene (Table 2). In conclusion, we carried out the addition of the dialkylthiophosphorous acids and the ethyl ester of ethylphosphinous acid to the ethyl ester of vinylphosphinic acid.*

As shown by our previous investigations [3], vinylphosphinic ester possessed definitely expressed electrophilic properties, thanks to which it had the capacity for addition reactions of the nucleophilic reagents and for the diene synthesis [4].

Using the alkali metal alcoholates as catalysts, we were able to add to them the dialkylphosphorous acids, ammonia and amines [5], hydrogen sulfide and mercaptans [4], and malonic, acetoacetic, cyanoacetic esters and their alkyl derivatives [6].

Because of these reactions, which we called phosphonethylation reactions we discovered the possibility of obtaining a whole series of new types of phosphinic acid derivatives. Continuing these investigations, we carried out the addition of diethylthiophosphorous acid, n-dibutylthiophosphorous acid and the ethyl ester of ethylphosphinous acid to the ethyl ester of vinylphosphinic acid. The reactions were carried out with equimolar quantities of reagents in the presence of sodium alcoholates, and proceeded very readily, accompanied by a considerable evolution of heat. For the dialkylthiophosphorous acids the course of the reaction can be represented by the equation

$$CH_2{=}CH{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + (RO)_2PSH \xrightarrow{RONa} (RO)_2\overset{S}{\overset{\|}{P}}CH_2CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2.$$

The reaction with the ethyl ester of ethylphosphinous acid proceeds similarly.

Two of the first addition products, 1-diethylphosphon-2-diethylthiophosphonethane and 1-diethylphosphon-2-n-butylthiophosphonethane, are colorless, rather mobile liquids with disagreeable odor; the odor of the ethyl ester of β-diethylphosphon-ethyl-ethylphosphinic acid was much weaker and less disagreeable (Table 3).

EXPERIMENTAL

General Method of Carrying Out Addition Reactions

A solution of the suitable sodium alcoholate (see theoretical part) in a solution of anhydrous alcohol was added dropwise to the reaction mixture, which consisted of equimolar quantities of unsaturated nitrile or vinylphosphinic ester (6-10 g) and dialkylthiophosphorous acid or ester of phosphinous acid (from 5 to 10 g), in a small round-bottomed flask, connected to a reflux condenser and dropping funnel. It should be noted that the presence of even small quantities of moisture in one of the reagents, or in the alcohol used for production of the alcoholate, severely retards the course of the addition reactions. The reaction generally does not proceed with a considerable quantity of moisture in the reaction mixture.

* M. M. Zakharov participated in the accomplishment of this part of the work.

The addition of the alcoholate solution was carried out very slowly and carefully, cooling the flask with cold water. On carrying out the reaction rapidly the evolution of heat, especially in the case of acrylonitrile, is so strong that it leads to a vigorous effervescence of the reaction mixture and to formation of resinous products. In these instances, the reactions should be carried out in the presence of solvents. After addition of the alcoholate necessary for completion of the reaction (absence of evolution of heat – check by thermometer) the reaction mixture was heated for half an hour on the water bath, and further vacuum distilled from an Arbuzov flask. Two distillations are sufficient for obtainment of a pure product.

SUMMARY

1. The addition of a series of dialkylthiophosphorous acids and acid esters of phosphinous acids to unsaturated nitriles – nitriles of acrylic, metacrylic and vinylacetic acids – was carried out. The addition products: the nitriles of β-dialkylthiophosphonpropionic, n-isobutyric and n-butyric acids were obtained in a 60-70% yield. The esters of ethyl-β-(cyanoethyl)-, phenyl-β-(cyanoethyl)-, ethyl-β-(cyanopropyl)-, ethyl-(α-methyl-β-cyanoethyl)-phosphinic acids were obtained in yields of 50-60%.

2. The phosphonethylation of diethylthiophosphorous and n-dibutylthiophosphorous acids and the ethyl ester of ethylphosphinous acid was carried out. The yield of the corresponding dialkylphosphon- and dialkylthiophosphonethanes amounted to 60-66%.

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** See Consultants Bureau Translation, page 855.
*** See Consultants Bureau Translation, page 273.
**** See Consultants Bureau Translation, page 227.

STUDY OF A SULFONATION REACTION

XXXV. PRODUCTION OF THE DI- AND TRISULFOCHLORIDES OF TOLUENE

A. A. Spryskov and T. I. Yakovleva

The 2,4-disulfochloride of toluene was obtained by Gnehm and Forrer [1] by heating the potassium salt of 2,4-toluenedisulfonic acid with phosphorus pentachloride. This method consisted of three operations: sulfonation, formation and separation of the salt, and conversion of the salt to the chloride. Pollak and coworkers [2] obtained 2,4-toluenedisulfochloride by heating toluene with an excess of chlorosulfonic acid at 140-150° for 5 hours. However, the product was separated as a viscous cinnamon-colored oil, which solidified after 24 hours, and only after recrystallization from ether was obtained with a m.p of 52°. The yield was not specified. Earlier the dichloride was obtained by Fahlberg [3] in a similar way. Other data in the literature on the production of the dichloride relate either to its obtainment from the potassium salt of toluenedisulfinic acid [4] or by the action of chlorosulfonic acid on the disulfofluoride [5].

Toluenetrisulfochloride-2,4,6 was obtained by heating the potassium salt of the 2,4-toluenedisulfo acid with chlorosulfonic acid at 240°, by conversion of the sulfo acid first to the barium salt, and then to the potassium salt, and by treatment of the latter with phosphorus pentachloride [6].

There are no other methods of production of toluenesulfo acid or its chloride in the literature, unless we consider the oxidation of 2,4,6-trimercaptotoluene to the trichloride by chlorine [7].

The purpose of the present work was also the development of methods of preparation of the di- and trisulfochlorides of toluene, which as far as possible would readily give products in the pure form. Some of the properties of the polysulfochlorides were also studied.

EXPERIMENTAL

Preparation of 2,4-toluenedisulfochloride. p-Toluenesulfochloride with a m.p. of 68.5-69.5° (according to literature data, m.p. 69° [8]), which was recrystallized with carbon from ether, was the starting material for preparation of 2,4-toluenedisulfochloride. 4 g of the monosulfochloride was heated with 11.5 ml of distilled chlorosulfonic acid at 145-147°. Heating of the mixture at about 145° was continued for 10 minutes. After definite intervals samples were withdrawn by pipette and poured into water. As a rule, the oil which separated quickly crystallized, the product was filtered off, washed on the filter with water, and then its melting point was determined, according to which we could judge the purity of the dichloride obtained, i.e., whether the sulfonation reaction had gone to completion.

The experimental results showed that a half hour of the heating was entirely sufficient for complete conversion of the monosulfochloride to the dichloride, since during this time a product with a m.p. of 52.4-52.8° was obtained. Further heating deteriorated the quality of the product, for its melting point systematically decreased, and after a 9-hour heating a dichloride with a m.p. of 50.9-51.2° was obtained. Thus, the experiments showed that we obtained the completely pure 2,4-disulfochloride of toluene without additional purification. (The melting point of the dichloride, according to literature data, was 52-54°). In another experiment a 3.58 g (52%) yield of the dichloride with a m.p. of 52-52.5° was obtained from 4.56 g of the monochloride and 13 ml of chlorosulfonic acid. The other 48% of the product remained unseparated as the sulfo acids, which formed due to the equilibrium of the dichloride with the sulfo acid, in the presence of sulfuric and chlorosulfonic acids, and which dissolved in water on decomposition of the reaction mixture on ice. It is known also that if there is a mixture of sulfo derivatives in the reaction substance, then the composition of the mixture of the individual chlorides formed does not differ from the composition of a mixture of free sulfo acids, because of the indicated equilibrium between the sulfo acid and its acid chloride [9]. Thus, the sulfonation proceeds quantitatively, but the dichloride yield depends on an excess of chlorosulfonic acid used in the reaction.

The experiments showed also that it is impossible to introduce a third sulfo-group into the toluene molecule by means of chlorosulfonic acid even at a temperature close to its boiling point.

The solubility of 2,4-toluenedisulfochloride at 20 ± 0.1° was determined in a somewhat modified Pavlevsk apparatus by keeping it in the thermostat for 1 and 4 hours. According to the determinations, 100 g of solution contained 73.5 g of the dichloride (average of 73.5-and 73.7).

Preparation of 2,4,6-toluenetrisulfochloride. The trisulfochloride was obtained by sulfonation of the 2,4-disulfochloride with fuming sulfuric acid by heating the components in a sealed tube. After heating, the tube was opened, chlorosulfonic acid was added to the mixture, the tube was heated again for ½ hour at 145-148°, and then the sulfo mixture was cooled and poured onto ice. The trichloride which precipitated was filtered off, washed, dried, and then its melting point was determined, which showed the degree of sulfonation of the disulfone to the trisulfo acid and the purity of the product.

From the results of the experiments it follows that for sulfonation we can use fuming sulfuric acid with a free sulfuric anhydride content from 30 to 60% in the quantity of 1 ml per 1 g of the dichloride. At a temperature of about 160° the reaction proceeds slowly and is completed after 25 hours. At a temperature of 180° for 4 hours the reaction proceeds quantitatively, since extremely pure trisulfochloride with a m.p. of 158-161° was formed. The trisulfo acid forms during the first stage of the reaction and only on heating with chlorosulfonic acid does the trichloride form. The trichloride yield depends on the quantity of chlorosulfonic acid introduced. The yield amounted to 54% on introduction of 24 ml of chlorosulfonic acid into a mixture of 6 g of the dichloride and 6 ml of 38% fuming sulfuric acid. The other 46% consisted of the 2,4,6-trisulfo acid, which remained in solution on separation of the chloride.

The toluenetrisulfochloride can also be produced by sulfonation of the monotoluenesulfochloride. A product with a m.p. of 157-159° was obtained by heating 2 g of p-toluenesulfochloride with 2 ml of 67% fuming sulfuric acid for 4 hours at 180°, with subsequent treatment by chlorosulfonic acid.

Properties of 2,4,6-toluenetrisulfochloride. Of the properties of 2,4,6-toluenetrisulfochloride, in the chemical literature it was indicated only that it has a m.p. of 153°, is very difficultly soluble in boiling ether and crystallizes from chloroform. The trichloride which we obtained after 2 recrystallizations from glacial acetic acid had a m.p. of 162°. Thus, Klason obtained not by any means pure trichloride [5], and the melting point which he cited was lower by 9° than that of the product which we obtained.

Determination of sulfur, according to Carius, gave the following results:

0.1053 g sub.: 0.1866 g $BaSO_4$. 0.1109 g sub.: 0.1970 g $BaSO_4$. Found %: S 24.37, 24.35. $C_7H_6O_6S_3Cl_2$. Calculated %: S 24.82.

A study of the solubility of the product with a m.p. of 156-159° showed the following. The trichloride dissolved poorly in the cold and well on heating in benzene, toluene, gasoline and glacial acetic acid. It was highly soluble in dichloroethane and in chloroform. It dissolved in chlorosulfonic acid, especially on heating. A substance with a m.p. of from 157 to 162° crystallized from all of these solvents.

The solubility of the trichloride in ether at 20 ± 0.1° (in a modified Pavlevsk apparatus with maintenance in a thermostat for 1 and 4 hours): 100 g of solution contained 0.73 g of the trichloride (rounded off from 0.725 and 0.728).

Thus, the solubility of the dichloride was approximately 100 times greater than that of the trichloride.

SUMMARY

1. A method of quantitative sulfonation of p-toluenesulfochloride to 2,4-toluenedisulfochloride, which readily gave a completely pure product in one operation, was proposed.

2. A method of quantitative sulfonation of 2,4-toluenedisulfochloride and p-toluenemonosulfochloride to 2,4,6-toluenetrisulfochloride, also giving a pure product in one operation, was developed

3. The properties of the 2,4,6-trichloride were studied. Its melting point was found to be more accurate, proving to be higher by 9°, than that indicated in the literature. Its solubility in different solvents was studied qualitatively and was determined quantitatively in ether at 20°.

The solubility of 2,4-toluenedisulfochloride in ether was determined at 20°.

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* See Consultants Bureau Translation, page 727.

SYNTHESES ON THE BASIS OF ANABASINE

X. CYANOETHYLATION OF ANABASINE

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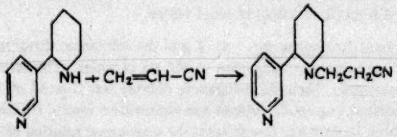
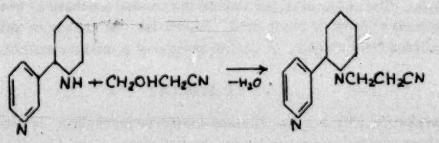
Syntheses on the basis of anabasine have led to a whole series of pharmacologically interesting substances [1]. It is necessary to consider the N-alkyl derivatives of anabasine as the most important of them [2]. Examinations of these compounds showed that they are less toxic than is anabasine, and at the same time stimulate respiration and improve the functioning of the heart [3]. In connection with this, further development of these syntheses in the direction of production of functionally-substituted alkyl derivatives of anabasine is of interest.

We studied the reactions of anabasine with acrylonitrile and ethylenecyanohydrin. The systematic study of the addition reaction of different compounds containing a mobile hydrogen atom to the double bond of acrylonitrile was begun and continued by Terentyev and his coworkers [4]. Thanks to this reaction, at the present time widely known by the name of cyanoethylation, the β-substituted derivatives of propionitrile and their transformation products became available, many of which began to acquire practical value [5].

We studied the reaction of anabasine and acrylonitrile by heating them in sealed tubes, in which the largest yield of the reaction product – N-(β-propionitrile)-anabasine (80.9%) – was obtained at temperatures of 145-150° with a heating time of 6 hours. Higher yields (91.3%) were obtained by refluxing (75-80°) mixtures of anabasine and acrylonitrile in aqueous solutions. N-(β-propionitrile)-anabasine formed quantitatively on carrying out the reaction under analogous conditions, but in the presence of catalytic quantities of alkali hydroxides (in all the above-mentioned experiments a 5% excess of acrylonitrile as compared to the calculated was used):



The structure of the product obtained was confirmed by oxidation with potassium permanganate, by which nicotinic acid and anabasine were formed. Moreover, an attempt to carry out the reaction of acrylonitrile with N-methanabasine gave negative results. N-(β-propionitrile)-anabasine was obtained also from anabasine and ethylenecyanohydrin:



EXPERIMENTAL

1. Reaction of anabasine and acrylonitrile in the presence of alkali hydroxides. 35.40 g (0.21 mole) of anabasine and 0.60 g of sodium hydroxide were dissolved in 75 ml of water (until formation of a homogeneous mixture), and with stirring 15 ml (0.23 mole) of acrylonitrile was added. The reaction took place with a small evolution

of heat, and the solution separated at once into layers. Then the mixture was refluxed at 50-60° for 30 minutes. After cooling, the reaction product was extracted with ether. The ether solution was dried over calcined potash, and after removal of the solvent the residue was vacuum distilled. The yield of N-(β-propionitrile)-anabasine mounted to 95-98%.

2. Reaction of anabasine with ethylenecyanohydrin. 36.00 g (0.22 mole) of anabasine, 16.00 g (0.22 mole) of ethylenecyanohydrin and 2 g of tin powder [6] were heated in a sealed tube on the oil bath at 150-170° for 4 hours. After cooling, the reaction mixture was dissolved in ether and dried over potash. After removal of the solvent the residue was vacuum distilled. N-(β-Propionitrile)-anabasine was separated in a quantity of 28.51 g (59.7%).

The N-(β-propionitrile)-anabasine was a viscous, colorless liquid with a b.p. of 163-165° (0.5 mm), 172-173° (2 mm); 212-215° (10 mm); it was poorly soluble in water and highly soluble in organic solvents – alcohol, acetone, chloroform, ether and benzene: n_D^{20} 1.5320, $[\alpha]_D$ −36.77° (in alcohol).

The following salts were formed.

The monopicrate, m.p. 102-104°, precipitated on addition of a water-alcohol solution of the calculated quantity of picric acid to an alcoholic solution of the base.

2.321 mg sub.: 0.404 ml N_2 (20°, 709 mm). 2.900 mg sub.: 0.509 ml N_2 (20°, 701 mm). Found %: N 18.71, 18.85. $C_{19}H_{17}N_9 \cdot C_6H_3O_7N_3$. Calculated %: N 18.90.

The dipicrate, m.p. 183-184° (with decomposition), was a hygroscopic compound which deliquesced in the air.

The dihydrochloride, m.p. 212°, was precipitated by mixture of acetone solutions of the base and hydrogen chloride, and crystallized from mixtures of acetone and alcohol as coarse, hexagonal prisms.

0.2096 g sub.: 12.7 ml 0.1125 N $AgNO_3$. 0.5118 g sub.: 31.1 ml 0.1125 N $AgNO_3$. 2.705 mg sub.: 0.358 ml N_2 (22°, 727 mm). 2.716 mg sub.: 0.353 ml N_2 (19°, 730 mm). Found %: Cl 24.16, 24.16; N 14.65, 14.59. $C_{19}H_{17}N_9 \cdot 2HCl$. Calculated %: Cl 24.60; N 14.59

The dihydrobromide, m.p. 228°, crystallized from an alcohol-acetone solution of the base, acidified to Congo-red with an aqueous solution of hydrogen bromide.

The diiodoethylate, m.p. 247-248°, precipitated after 24 hours from an acetone solution of a mixture of 7.15 g (0.03 mole) of the base and 6 ml (0.07 mole) of ethyl iodide.

3. Oxidation of N-(β-propionitrile)-anabasine. a) 1 g of the substance, dissolved in 50 ml of water, was mixed with a solution of 6.5 g of potassium permanganate in 200 ml of water. The solution was heated on the water bath until it was completely decolorized. Then the manganese dioxide was filtered off and washed repeatedly with hot water. The filtrate was evaporated to a small volume and neutralized toward litmus with a 10% solution of hydrochloric acid. The amino acid which formed was precipitated by a saturated solution of copper acetate. The cupric salt was filtered off and decomposed by hydrogen sulfide. After separation from the copper sulfide, the mother liquor was evaporated to dryness. After recrystallization from a small quantity of hot water, the residue (0.50 g – 87%) had a m.p. of 231-232°. A test sample of a mixture with nicotinic acid melted at 230-232°.

b) 15.8 g of potassium permanganate in 350 ml of water was added gradually to 3.60 g of the substance in 125 ml of a 5% solution of sulfuric acid. The mixture was allowed to stand for 1 hour and was then filtered off from the manganese dioxide. The filtrate was alkalized with 20% sodium hydroxide and extracted with ether. The ether solution was dried over potash. After removal of the solvent the residue (anabasine) was dissolved in a small amount of water and added to an aqueous solution of picric acid. In addition, the anabasine picrate which precipitated, m.p. 197-198°, was recrystallized from alcohol. A control sample of a mixture melted also at 197-198°.

SUMMARY

1. The reactions of anabasine with acrylonitrile and ethylenecyanohydrin, by which N-(β-propionitrile)-anabasine was formed and characterized, were studied for the first time.

2. It was shown that N-(β-propionitrile)-anabasine was formed quantitatively from anabasine and acrylonitrile in aqueous solutions in the presence of catalytic quantities of alkali hydroxides.

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* See Consultants Bureau Translation, page 1295.

TRANSFORMATION AND SYNTHESIS OF CARBOHYDRATES

XII. INVESTIGATION IN THE FIELD OF REDUCTION OF ALDONOLACTONES

V. M. Berezovsky

Fischer's method [1], consisting of the reduction of the lactones of the aldonic acids with alkali metal amalgams, is one of the methods for the synthesis of monoses. The reaction is carried out with 2.5-3% amalgam (solid) at a pH of 3-3.5 [2] (or at a pH corresponding to a slight gray color of Congo paper [3]). Consequently, on reduction by solid sodium amalgam, the reaction rate is especially high at first, and the regulation of the acidity of the medium within the required pH limits is connected with difficulties [2, 3], even with circulation of the solution [4].

In the present work both the direct electroreduction reaction of the aldonolactones to aldoses [5] and the chemical reduction reaction (not direct electrolytic) by low-percentage (about 0.1%) liquid alkali metal amalgams were studied. These reduction methods permit us to carry out the reaction under mild, strictly controlled conditions.

It should be noted that in many instances complete analogy between electrolytic reduction at a mercury cathode and reduction by sodium amalgam is observed [6]. However, V. V. Levchenko [7], in a series of instances with the renewal of the mercury cathode, showed that the given analogy was not always observed.

The reduction reaction of the aldonolactones by sodium amalgam is carried out at a pH below 7; at a pH above 7 further reduction of aldoses to monatomic alcohols occurs, and in addition, hydrolysis of the aldonolactone takes place. Sorbitol was formed (with an admixture of mannitol) [8] by the electrolytic reduction of glucose at a pH of 8.2-10.85; this process takes place also at a pH of 7 [9]. For the electroreduction of aldoses to monatomic alcohols, apart from the mercury cathode, high yields were obtained by the use of amalgamated lead; poorer yields were obtained at amalgamated and non-amalgamated cathodes of Cd, Zn, Al and Ni [8]. A cathode of Al—Ni alloy gave a high yield of the monatomic alcohol. However, the reduction of an aldose does not take place at Cu and Fe cathodes [8].

A different type of reduction reaction was observed for the aldonolactones at a pH below 7. At the mercury cathode this reaction gives a high yields of aldoses. However, our attempt to carry out the reaction at cathodes of other metals was unsuccessful. Unlike the electrolytic reduction reactions of the aldoses to monatomic alcohols, reduction of aldonolactones to aldoses by other metals than mercury, with high (Pb, Sn, Zn) or low (Ni) overvoltages, and also at the Cu-cathode, did not occur. At amalgamated Sn, Zn, Cu and Ni cathodes, for example, arabinose could be obtained in a low yield; with amalgamated Pb the arabinose yield increased to 12-22%.

On reduction of the aldonolactones at the mercury cathode considerable fluctuation of the aldose yields was observed. As a result of a study of this phenomenon, we found a relationship between the size of the aldose yields and the mobility of the mercury cathode. High and stable yields of the aldoses, 60-67%, occurred with vigorous stirring of the cathode mercury; the yields amounted to only 2.5-18% (for arabinose) with a stationary mercury cathode. Consequently, with a stationary mercury cathode surface (and consequently, an amalgamated cathode) the course of the reaction is retarded or even stopped altogether.

The reduction reaction was also studied in an electrolyzer with a diaphragm, the characteristic of which was stability, permitting a continuous exchange of the cathodic mercury, i.e., the constant removal of the sodium amalgam which formed, and the creation of conditions for the appearance of catalytic properties of the pure mercury cathode. The reduction reaction of arabonolactone, without renewal but with vigorous stirring of the cathodic mercury, proceeded with a yield of 59%. With a stationary cathode, without stirring and without renewal of it, i.e., under the conditions of slight reaction of sodium amalgam, the yield amounted to 10% all told. The reduction reaction ceased altogether with renewal of the mercury cathode, with rapid flow of the mercury.

Thus, the complete absence of an analogy between the reduction of aldonolactones by alkali metal amalgams and the reduction at a pure mercury cathode can be established. Electrolytic reduction of the aldonolactones to aldoses at cathodes of different metals, and at a genuine mercury cathode, does not take place; the cathodic mercury does not catalyze this reaction. In the presence of alkali metal ions the reduction reaction proceeds at the mercury cathode due to the formation of alkali metal amalgams.

EXPERIMENTAL*

Preparation of Aldonolactones

d-Arabono-γ-lactone was obtained according to [10].

d-Ribono-γ-lactone. 100 g of cadmium ribonate (recrystallized twice) was dissolved in 600 ml of water, and the solution was saturated with hydrogen sulfide until complete precipitation of cadmium sulfide. After filtration the solution was vacuum evaporated to a syrup, which was kept in vacuo at 90-95° for 1 hour in order to complete the lactonization. 56.6 g of a syrup of d-ribono-γ-lactone (84%), which crystallized on standing, was obtained. The crystalline substance was treated with 170 ml of ethyl acetate at 40°; with cooling, the crystals were filtered off and washed with ethyl acetate. 24 g of crystalline d-ribono-γ-lactone, with a m.p. of 76-77°, was obtained. A somewhat greater quantity of the lactone separated from the mother liquor on standing.

d-Glucono-γ-lactone was obtained from calcium gluconate by treatment with oxalic acid, followed by concentration and lactonization by the usual method.

Reduction of the Aldonolactones by Low-Percentage Sodium Amalgam (Not Direct Electroreduction)

The apparatuses which were used for the reduction consisted of a reactor and an electrolyzer connected to each other. The low-percentage, liquid, sodium amalgam (below 0.1%), obtained electrolytically by the usual method, was circulated continuously between the reactor and the electrolyzer; after use of the freshly-obtained amalgam in the reactor for reduction of the lactone, the mercury was returned to the electrolyzer for regeneration of the amalgam.

The cylindrical type apparatus consisted of two parts: the reactor, an open glass cylinder inserted inside the glass vessel at a height of 20 mm from the bottom, and the electrolyzer, located in the space formed by the cylinder and the glass vessel. The cathodic mercury was poured in to a height of 25 mm and formed an hydraulic seal 5 mm high. By means of stirring the mercury, a continuous exchange between the reaction and the electrolytic compartments occurred.

The chamber type apparatus consisted of a rectangular-shaped compartment divided into two chambers — a reactor and an electrolyzer — by a partition which did not reach to the bottom. The cathodic mercury was poured into the apparatus to 10 mm above the lower level of the partition, forming a hydraulic seal. By means of alternate tilting and raising of one side of the apparatus, the amalgam was poured from the electrolyzer chamber to the reaction chamber and back, all the time subjecting it to decomposition and regeneration. 15 tiltings per 1 minute were carried out.

About 27-45 g of the aldonolactone, as a 6-10% aqueous solution which was stirred intensely at 12-16°, was used for the reduction. The acidity of the solution was maintained within the pH limits of 3-4 by addition of a 20% solution of sulfuric acid, depending on the extent of reduction. The reduction was completed (after 1-2 hours), after which the aldose content in solution ceased to increase (analysis carried out for reducing substances); control reactions were carried out also according to the decrease of the quantity of lactone (hot and cold titration with an alkali solution). The generator of the amalgam was supplied with a current of 10 amp at a voltage of 4.5 V.

On reduction of d-glucono-γ-lactone by a low percentage, sodium amalgam, a yield of 46.5-48% d-glucose was obtained, a yield of about 45% of d-ribose was obtained from d-ribono-γ-lactone (syrup), and a yield of 70% of d-arabinose was obtained from d-arabono-γ-lactone (crystalline).

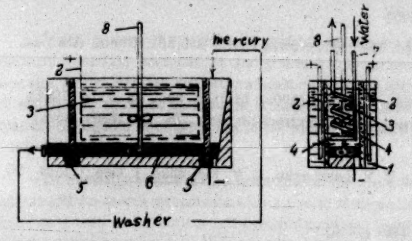
Reduction of the Aldonolactones at the Mercury Cathode without Renewal and With Continuous Renewal of the Mercury (Direct Electroreduction)

Reduction of the aldonolactones, without renewal and with continuous renewal of the mercury cathode, was studied in a modified Levchenko apparatus. The electrolyzer which we used consisted of three chambers: two lateral anode chambers 1, in which the lead anode 2 was located, and a middle cathode chamber 3, which was separated from the anode chamber by a double diaphragm 4; the area of the diaphragm amounted to 1 dm^2. The cathode chamber had a slit opening in the lower part with a hydraulic seal 5, through which the cathode 6 mercury was admitted and flowed. A cooling coil 7 and a stirrer 8, which stirred only the aqueous layer of the catholyte, or, depending on the conditions of the experiment, also simultaneously stirred the cathodic mercury (see Figure), were located in the cathode chamber.

* With the participation of V. S. Varkov.

The mercury which flowed from the electrolyzer proceeded into a column filled with a 10% solution of nitric acid, passing through which it proceeded into a column with running water. The pure mercury, washed free from amalgam, again entered into the electrolyzer.

The catholyte consisted of an aqueous solution which contained 10% sodium sulfate and 10% aldonolactone. 10% sulfuric acid was used as the anolyte. The pH of the catholyte was maintained with the limits of 3-4.5 during the reaction by addition of 20% sulfuric acid.



Electrolyzer for reduction with continuous renewal of the mercury cathode. 1) Anode chamber; 2) anode; 3) cathode chamber; 4) diaphragm; 5) hydraulic seal; 6) mercury cathode; 7) cooling coil; 8) stirrer.

In the experiments with renewal of the cathode mercury, the rate of flow of the mercury through the electrolyzer amounted to 1.2 kg per minute, i.e., the rate of renewal supplied 186 kg/dm^2 per hour. It was possible to carry out the electrolytic reduction in the apparatus also without renewal of the mercury (on the same cathode surface of 38.6 cm^2). The experiments were carried out at a current density of 5.2 amp/dm^2 and 12-16°.

The results of the experiments were as follows: a) no reduction of the aldonolactones occurred at a pH below 7 at a pure mercury cathode (continuous renewal); b) reduction took place with a small yield (10% yield of d-arabinose) at a stationary mercury cathode (without renewal and without stirring of the cathodic mercury); c) by vigorous stirring of the cathode mercury (without renewal) reduction occurred with a high yield of aldose [(59% yield of d-arabinose from the d-arabono-γ-lactone (syrup), and 39% d-ribose from d-ribono-γ-lactone (syrup)]

A series of experiments was conducted in the electrolyzer with cylindrical diaphragm walls at a current density of 9.3 amp/dm^2, a pH of 3.2-4.6, and a temperature of 12-16°, without renewal of the cathodic mercury. d-Arabinose was obtained in a yield of 10-18% (by vigorous stirring of the catholyte) and 2.5% (by slight stirring of the catholyte) at a stationary mercury cathode. d-Arabinose was obtained in a yield of 60-67%, with vigorous stirring of the cathode mercury.

Concerning the Stability of Aldonolactone Solutions

A 10% aqueous solution of d-arabono-γ-lactone was maintained in the thermostat for 2 hours, and then analyzed for aldonic acid content (cold titration with 0.1 N sodium hydroxide solution) and lactone content (hot titration with 0.1 N sodium hydroxide solution). In the absence of alkali, the lactone solution was stable and did not open within the range of 0-30°, a small opening of the lactone (about 2%) was observed at a higher temperature.

The lactone hydrolyzed readily in an alkaline medium. In the presence of alkali corresponding to 95% of the quantity of the lactone, hydrolysis occurred after 35 minutes at 10°, and after 8 minutes at 24°. In the presence of a constant small excess of alkali (concentration about 0.015%) complete hydrolysis of the lactone occurred after 95 minutes at 10°, and after 35 minutes at 24°. Under the conditions of the electrolysis, because of the presence of a local zone with an alkaline reaction near the surface of the amalgam, partial hydrolysis of the lactone occurred. The hydrolysis increased with an increase of the temperature, and, for example, the yield of arabinose decreased by 20% at 20-21°, and by 65% at 25-26°.

SUMMARY

1. It was shown that the reduction reaction of the lactones of aldonic acids proceeds with the participation of amalgams with low (below 0.1%) alkali metal content.

2. It was found that stirring the cathode mercury favors the production of high and stable yields of aldoses.

3. The absence of an analogy between the reduction of aldonolactones to aldoses by alkali metal amalgams and reduction at a pure mercury cathode was established.

4. The reduction reaction of the aldonolactones to aldoses at the mercury cathode or at amalgamated cathodes of other metals, in the presence of alkali metal ions, proceeds only to the extent that the low-percentage alkali

metal amalgams which form participate in the reduction reaction, due to which reduction of the aldonolactones to aldoses also occurs at a pH below 7. Reduction does not occur at a pure mercury cathode (by continuous renewal of the mercury) or at Ni, Cu, Sn, Pb and Zn cathodes.

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** See Consultants Bureau Translation, page a-93.

INVESTIGATION IN THE FIELD OF CYANIN DYES

V. SYNTHESIS OF N-ARYLQUINALDINE QUATERNARY SALTS AND THEIR TRANSFORMATIONS [1]

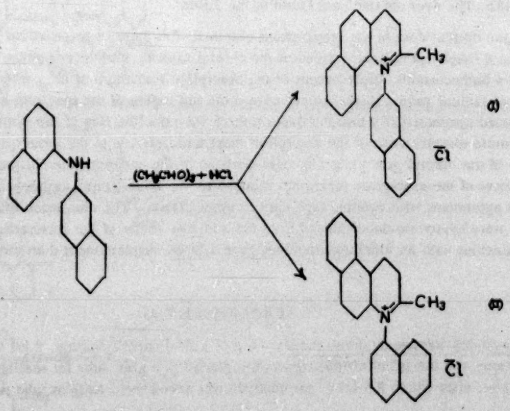
G. T. Pilyugin

Investigations of the primary aromatic amines by ortho-cyclization were known at the time when Skraup synthesized quinoline from aniline and glycerin in the presence of sulfuric acid [2], and Doebner and Miller studied the reaction of the primary aromatic amines with acetic anhydride and paraldehyde under fixed conditions, as a result of which they obtained quinaldine, a homolog of quinoline [3]. The syntheses of Skraup and Doebner-Miller became classics in organic chemistry and found wide application in scientific investigations and in the development of industrial organic synthesis.

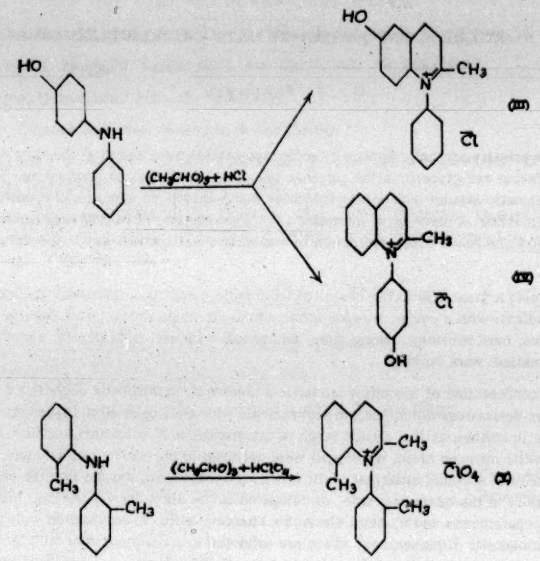
Its quaternary salts play a great role in the chemistry of quinoline and its derivatives, which contain aliphatic and aliphatic-aromatic radicals with a cyclic nitrogen atom, which are more active forms than the free bases. However, in theory and practice, until recently, among them, compounds with aryl radicals with a cyclic nitrogen atom, which still had not been studied, were lacking.

We showed that on condensation of secondary aromatic amines with paraldehyde under fixed conditions, cyclization to the quinaldine derivatives which contain aryl radicals with a nitrogen atom [4] occurs. With the cyclization of secondary aromatic amines, at first a wide range of investigations of quinoline derivatives which contain an aryl grouping with a cyclic nitrogen atom, which still were unknown to chemistry, was assumed. The investigations carried out on the series of arylated quaternary salts which we synthesized, showed that the presence of aryl radicals increases the activity of the quaternary salts, as compared to the alkyl derivatives [5]. Moreover, the aryl grouping, as shown by other parameters and by other electronic characteristics, in comparison with the alkyl grouping, gives rise to various intramolecular displacements, which are reflected to a certain extent both by the activity of the molecule as a whole, and by the activity of the individual functional groups. An interesting aspect of the research is the fact that cyclization of amines of asymmetric structure may result in molecular isomeric transformations, which may occur as the result of changes in the conditions of cyclization.

We carried out the condensation of α,β-dinaphthylamine, p-hydroxydiphenylamine and o,o-ditolylamine with paraldehyde in an acid medium, in the presence of nitrobenzene, as a result of which the quinaldine derivatives were obtained. Moreover, the cyclization reaction can proceed with the formation of such quaternary salts as:



However, as the experiments showed, under our conditions the reactions proceeded exclusively toward the formation of the quaternary salts: N-(β-naphthyl)-7,8-benzoquinaldine chloride (I), N-phenyl-6-hydroxyquinaldine chloride (III), and N-o-tolyl-8-methylquinaldine perchlorate (V) No other isomeric reaction products were observed.



On condensation of the salts with ethyl o-formate carbocyanin dyes were obtained, with spectral absorption curves having sharp maxima characteristic of the cyanines. The resulting quaternary salts were heated with orthoformic ester, as a result of which trimethenylcyanines of symmetrical structure were obtained [6].

On condensation of the salts with the iodoethylate of 2-β-acetanilinovinylbenzothiazole and with the iodomethylate of 2-β-acetanilinovinyltrimethylindolenine, trimethenylcyanines of asymmetrical structure were obtained [7]. Moreover, the condensation of the salts with p-dimethylaminobenzaldehyde was carried out with production of styryl derivatives [8]. The dyes obtained are listed in the Table.

Comparing the optical data of the preparations obtained with those of preparations having a different structure, it was seen that the β-naphthyl radical, instead of the o-tolyl radical, introduced symmetrically at the hetero nitrogen atom, showed a bathochromic displacement of the absorption maximum of the carbocyanine by 6 mμ [9], and relative to the ethyl radical gave a displacement toward the red region of the spectrum by 14 mμ [10]. The hydroxy-group, introduced symmetrically into the 6-position of the quinoline ring of the symmetrical carbocyanine, caused a bathochromic displacement of the absorption maximum relative to the unsubstituted carbocyanine by 12 mμ. Introduction of the methyl group into the meso-position of the carbocyanine chromophore caused a hypsochromic displacement of the absorption maximum relative to the unsubstituted carbocyanine chromophores. This was found to be in agreement with cyanine type dyes of other classes. The absorption maxima of the dyes of asymmetrical structure were hypsochromo-displaced from the additive values of the corresponding symmetrical dyes, whereupon the molecules with an indolenine nucleus gave a larger displacement than did those with a benzothiazole nucleus.

EXPERIMENTAL

N-(β-Naphthyl)-7,8-benzoquinaldine iodide. 5 g of α,β-dinaphthylamine, 2 ml of hydrochloric acid (d 1.19), 5 ml of benzene and 0.5 ml of nitrobenzene were placed in a glass tube for sealing. The mixture was cooled with ice water, after which 2.6 ml of paraldehyde was added to it, and the tube was sealed. The mixture

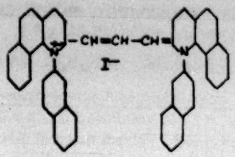
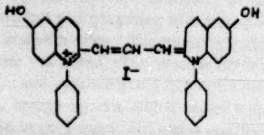
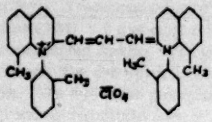
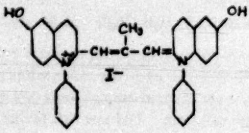
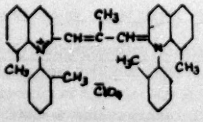
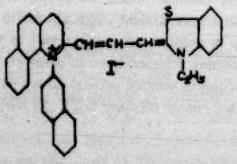
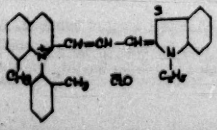
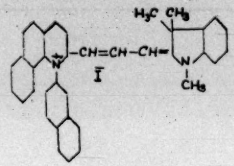
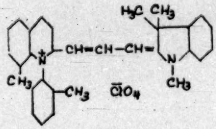
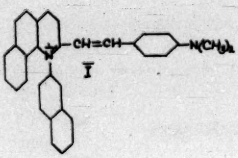
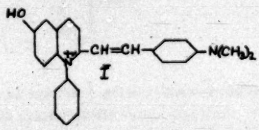
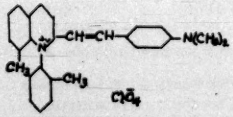
Test No.	Formulas of dyes	Absorption maximum (in mμ)
1	2	3
1		648
2		626
3		623
4		620
5		617
6		596
7		584

TABLE (continued)

1	2	3
8		584.5
9		565
10		550
11		542
12		546

was boiled on a water bath for 9-10 hours with periodic shaking. On cooling the reaction substance was treated repeatedly with small portions of ether until the ether was no longer colored. Then the quaternary salt was dissolved by heating on the water bath in 30-40 ml of alcohol, after which it was filtered. The alcoholic filtrate of the chloride salt was treated with a saturated solution of potassium iodide in order to convert the salt to the iodide. After addition of the potassium iodide the solution was boiled for 5 minutes, filtered hot and allowed to crystallize. The light-cinnamon colored salt precipitate which came down was filtered, washed several times with water and with ether, and dried in the air. After recrystallization from an alcohol-water mixture 2.2 g (26.6%) of the salt was obtained. The salt melted with decomposition at 226°.

Found %: I 28.16. $C_{24}H_{18}NI$. Calculated %: I 28.35.

N-Phenylhydroxyquinaldine iodide: 3 g of p-hydroxydiphenylamine, 3 ml of benzene, 1.5 ml of hydrochloric acid (d 1.19) and 0.5 ml of nitrobenzene were placed in a glass tube for sealing up, and cooled with ice water, after which 2.5 ml of paraldehyde was added, and the tube was sealed up. After heating the mixture on a boiling

water bath for 6-7 hours the reaction product was treated with ether until the latter was decolorized. Then the technical salt was dissolved in a small quantity of alcohol and filtered. 3 g of potassium iodide was added to the alcoholic filtrate, dissolved in 15 ml of water, and all were simmered for 10 minutes, after which a 3-fold volume of water and 1 g of activated carbon were added to the solution, and the substance was boiled again for 15 minutes. After hot filtration the light-yellow filtrate was evaporated to 100 ml; on cooling the quaternary salt was precipitated from it as light-orange needles. After recrystallization from an alcohol-water mixture the salt melted with decomposition at 178-180°. 0.8 g (13.7%) of the salt was obtained.

Found %: I 34.55. $C_{19}H_{16}ONI$. Calculated %: I 34.94.

N-(o-Tolyl)-8-methylquinaldine perchlorate. 3 g of o,o-ditolylamine, 3 ml of benzene, 3.6 ml of hydrochlorid acid (30%), 0.2 g of nitrobenzene and 2 ml of peraldehyde were heated in a sealed tube on a boiling water bath for 8-10 hours with frequent shaking. The condensation product was treated repeatedly with small portions of ether until the latter was decolorized; moreover, the reaction substance became very viscous, and after addition of a small quantity of alcohol and triturating with a glass rod, it crystallized. The salt precipitate was filtered, and washed with alcohol and with ether. The resulting technical quaternary salt was boiled in 500 ml of water to which 1 g of activated carbon was added. The aqueous salt solution was filtered hot, and by evaporation the quaternary salt was crystallized, and was subjected to purification several times until stable constants were obtained. The salt consisted of fine, orange crystals, which melted with decomposition at 180-181°; they were highly soluble in alcohol, slightly soluble in cold water, and highly soluble in hot water. The yield was 0.96 g (18.6%).

Found %: Cl 10.12. $C_{19}H_{18}O_4NCl$. Calculated %: Cl 10.33.

Bis-(N-β-naphthyl-7,8-benzoquinoline-2)-trimethenylcyanine iodide. 1 g of the quaternary salt of β-naphthylbenzoquinaldine iodide (2 M), 0.2 g of ethyl orthoformate (1 M) and 3 ml of pyridine were boiled on a paraffin bath for 30 minutes, with continuous shaking. The greater the extent of heating, the more intense became the green color of the reaction substance. The dye which formed after cooling was precipitated with ether, dissolved in alcohol and allowed to crystallize. The dye which precipitated was filtered, washed with ether and with a small quantity of alcohol, after which it was recrystallized from an alcohol-water mixture. The dye consisted of fine, dark-blue needles, and the alcoholic solution was an intense-green color. The m.p. was 270° (decomposition). The yield amounted to no more than 19%. The absorption maximum in a solution of ethyl alcohol was 648 mμ.

Found %: I 16.03, 16.21. $C_{49}H_{33}N_2I$. Calculated %: I 16.31.

Bis-(N-phenyl-6-hydroxyquinoline-2)-trimethenylcyanine iodide. 0.5 g of phenyl-6-hydroxyquinaldine iodide, 0.1 g of ethyl orthoformate, and 3 ml of pyridine were boiled on a paraffin bath for 30 minutes. The greater the extent of heating the more intense became the color of the solution. Further treatment was as described above. The yield of the technical dye was 30%. After recrystallization from an alcohol-water mixture 0.13 g (12.5%) was obtained. The absorption maximum of the dye in an ethyl alcohol solution was 626 mμ. The absorption curve of the dye, with a sharply expressed maximum, was typical of the cyanines.

Found %: I 20.71, 20.58. $C_{53}H_{37}O_2N_2I$. Calculated %: I 20.86.

Bis-(1-o-tolyl-8-methylquinoline-2)-trimethenylcyanine perchlorate. 0.5 g of the salt of 1-o-tolyl-2,8-dimethylquinoline perchlorate, 0.25 g of ethyl formate and 2 ml of pyridine were boiled moderately for 40 minutes, at which time the intensity of the color was gradually heightened. On cooling dye crystals separated, which were crystallized from an alcohol-water mixture. The dark-green crystals had a metallic luster, and a m.p. of 263° (decomposition). The alcoholic solution of the dye was an intense-blue. The yield amounted to 24.5%. The absorption maximum of the dye in an ethyl alcohol solution was 623 mμ.

Found %: Cl 5.79. $C_{37}H_{33}O_4N_2Cl$. Calculated %: Cl 5.87.

Bis-(N-phenyl-6-hydroxyquinoline-2-)-β-methyltrimethenylcyanine iodide. 1 g of the salt of phenylhydroxyquinaldine, 0.2 g of ethyl orthoacetate and 2 ml of pyridine were boiled for 2 hours on a paraffin bath. On cooling the resulting carbocyanine was treated as described above. After repeated crystallization from an alcohol-water mixture the yield was 12%. The m.p. was 201-202° (decomposition); the absorption maximum of the dye in an ethyl alcohol solution was 620 mμ, i.e., it was displaced toward the short-wave part of the spectrum relative to that of the dye which was unsubstituted in the meso-position by 6μ.

Found %: I 20.12, 20.26. $C_{36}H_{27}O_2N_2I$. Calculated %: I 20.39.

Bis-(1-o-tolyl-8-methylquinoline-2)-β-methyltrimethenylcyanine perchlorate. 0.3 g of the quaternary salt of 1-o-tolyl-2,8-dimethylquinoline perchlorate, 0.20 g of ethyl orthoacetate and 3 ml of pyridine were boiled for

2 hours. The dye was precipitated with ether. The dye powder which precipitated was filtered, washed with ether, dissolved in a small quantity of alcohol and precipitated with a potassium perchlorate solution, whereby the dye solution and the perchlorate solution were first heated to boiling. On cooling the solution the dye precipitated, was filtered, and washed with water and with ether, after which it was recrystallized twice from an alcohol-water mixture; it was a dark-violet, finely-crystalline powder with a metallic luster. The alcoholic solution of the dye was an intense-blue. The m.p. was 196-198° (with decomposition). The yield was 12.7%. The absorption maximum of the dye in an ethyl alcohol solution was 617 mμ, i.e., was displaced by 6 mμ toward the ultraviolet region of the spectrum relative to the dye which was unsubstituted in the polymethenyl chain.

Found %: Cl 5.88. $C_{38}H_{37}O_4N_2Cl$. Calculated %: Cl 5.74.

(N-β-Naphthyl-7,8-benzoquinoline-2)-(3-ethylbenzothiazole-2)-trimethenylcyanine iodide. 0.54 g of β-naphthylbenzoquinaldine iodide (1 mole), 0.5 g of the iodoethylate of 2-β-acetanilinovinylbenzothiazole (1 mole) and 3 ml of pyridine were simmered on a paraffin bath for 40 minutes. The dark-violet colored dye which formed on cooling was precipitated with ether, and crystallized from an alcohol-water mixture with slow cooling. The dye consisted of dark-violet crystals with a metallic luster. The m.p. was 235° (decomposition). The yield was 27%. The absorption maximum of the dye in an ethyl alcohol solution was 596 mμ, which was a displacement by 7 mμ toward the short-wave part of the spectrum from the additive maximum of the corresponding symmetrical dye.

Found %: I 19.74, 19.86. $C_{36}H_{27}N_2SI$. Calculated %: I 20.00.

(1-o-Tolyl-8-methylquinoline-2)-(3-ethylbenzothiazole-2)-trimethenylcyanine perchlorate. 0.4 g of o-tolyl-2,8-dimethylquinoline perchlorate (1.2 mole), 0.4 g of 2-β-acetanilinovinylbenzothiazole iodoethylate (1 mole) and 2.5 ml of pyridine were simmered on a paraffin bath for 50 minutes with periodic shaking. The dye which formed was recrytsallized from an alcohol-water mixture, after which it consisted of a finely-crystalline, dark-violet colored powder with a metallic luster, and melted with decomposition at 227-228°. 0.11 g (19%) was obtained. The absorption maximum of an ethyl alcohol solution of the dye was 584 mμ. The absorption maximum was displaced 6.5 mμ toward the ultraviolet region of the spectrum from the additive value of the corresponding symmetrical dye.

Found %: Cl 6.28. $C_{29}H_{27}O_4N_2SCl$. Calculated %: Cl 6.45.

(N-β-Naphthyl-7,8-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethenylcyanine iodide. 1 g of naphthylbenzoquinaldine iodide, 1 g of the iodomethylate of 2-β-acetanilinovinyl-3,3-dimethylindolenine and 3 ml of pyridine were boiled on a paraffin bath for 30 minutes. At the time of heating the substance was shaken periodically. The intensity of the color increased as the extent of heating increased. The carbocyanine which formed was precipitated with ether, dissolved in a small quantity of alcohol by boiling, and allowed to crystallize. The dye which came down was filtered, washed with ether and crystallized from alcohol. The m.p. was 261° (decomposition). The yield was 0.31 g (22.4%). The absorption maximum of an ethyl alcohol solution of the dye was 584.5 mμ, i.e., it was displaced by 12 mμ toward the short-wave part of the spectrum from the additive value of the corresponding symmetrical dye.

Found %: I 20.0, 19.82. $C_{37}H_{31}N_2I$. Calculated %: I 20.13.

(1-o-Tolyl-8-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethenylcyanine perchlorate. 0.5 g of the salt of 1-o-tolyl-2,8-dimethylquinoline perchlorate, 0.5 g of the iodomethylate of 2-β-acetanilinovinyl-3,3-dimethylindolenine and 2 ml of pyridine were boiled moderately under reflux for 30 minutes, on a paraffin bath. It was treated further as described above. After recrystallization from an alcohol-water mixture the dye consisted of fine needles, which melted with decomposition at 208-209°. An alcoholic solution of the dye had a reddish-violet color. 0.23 g (32.7%) was obtained. The absorption maximum in an ethyl alcohol solution was 565 mμ, which consisted of a displacement by 19 mμ into the ultraviolet region of the spectrum from the additive maximum of the symmetrical dyes.

Found %: Cl 6.44. $C_{31}H_{31}O_4N_2Cl$. Calculated %: Cl 6.69.

(N-β-Naphthyl-7,8-benzoquinoline-2)-p-dimethylaminostyryl iodide. 1 g of 1-β-naphthyl-7,8-benzoquinaldine iodide (1 mole), 0.33 g of p-dimethylaminobenzaldehyde (1 mole) and 4 ml of pyridine were condensed by boiling on a paraffin bath for 30 minutes, during which the substance was shaken periodically. The dye which formed was separated by precipitation with ether and washed until the ether was no longer colored. Then the styryl derivative was dissolved by boiling in a small quantity of alcohol, from which the dye precipitated on cooling. After recrystallization from alcohol the dye consisted of lustrous, violet crystals with a metallic luster. The m.p. was 252° (decomposition). The yield was 0.41 g (29.8%). The absorption curve had an indefinite form. The absorption maximum of the dye in an ethyl alcohol solution was 550 mμ.

Found %: I 21.62, 21.74. $C_{29}H_{27}N_2I$. Calculated %: I 21.94.

(N-Phenyl-6-hydroxyquinoline-2)-p-dimethylaminostyryl iodide. 0.5 g of the quaternary salt of phenylhydroxyquinaldine iodide, 0.20 g of p-dimethylaminobenzaldehyde, and 3 ml of pyridine were boiled on a paraffin bath for a period of 20 minutes with several drops of acetic anhydride, with periodic shaking. The intensity of the color increased as the extent of heating increased. After cooling the dye was precipitated with ether. The precipitated and washed styryl was dissolved by boiling in a small quantity of alcohol, filtered hot and allowed to crystallize. After recrystallization from a large quantity of an alcohol-water mixture the dye had stable analytical data and consisted of fine, dark-violet needles with a metallic luster. The m.p. was 208-209° (decomposition). The yield was 32%. The absorption maximum in an ethyl alcohol solution was 542 mμ.

Found %: I 25.37, 25.51. $C_{25}H_{23}ON_2I$. Calculated %: I 25.67.

(N-o-Tolyl-8-methylquinoline-2)-p-dimethylaminostyryl perchlorate. 0.4 g of the quaternary salt of 1-o-tolyl-8-methylquinaldine perchlorate, 0.20 g of p-dimethylaminobenzaldehyde, 2.6 ml of pyridine and several drops of acetic anhydride were boiled on a paraffin bath for 40 minutes, during which the substance was shaken periodically. On the next day the reaction product was treated with ether, the resulting dye powder was filtered, and washed with ether, with water and with a small quantity of alcohol. The styryl derivative was recrystallized from an alcohol-water mixture The dye consisted of fine, reddish-cinnamon colored crystals which melted with decomposition at 245°. The alcohol solution of the styryl was crimson-colored. 0.15 g (27%) was obtained. The absorption maximum in an ethyl alcohol solution was 546 mμ.

Found %: Cl 7.23. $C_{31}H_{27}O_4N_2Cl$. Calculated %: Cl 7.41.

We thank V. N. Tolmachev sincerely for participation in the determination of the absorption curves.

SUMMARY

1. Three, until now unknown quaternary salts, derivatives of N-arylquinaldines were synthesized: N-β-naphthyl-7,8-benzoquinaldine iodide, N-phenyl-6-hydroxyquinaldine iodide, and N-o-tolyl-2,8-dimethylquinoline perchlorate, from which 9 new symmetrical and asymmetrical carbocyanine structures and 3 styryl derivatives were obtained. Absorption curves were taken for all the preparations in an ethyl alcohol solution.

2. It was shown that the β-naphthyl, phenyl-, and o-tolyl radicals, introduced instead of the ethyl radical at the cyclic nitrogen atom, displaced the absorption maximum bathochromically.

3. Introduction of the hydroxy-group into the 6,6'-position of N-phenylquinocarbocyanine, bathochromically displaced the absorption maximum by 12 mμ, and the methyl group in the meso-position of the polymethenyl chromophore hypsochromically displaced the absorption maximum by a negligible amount.

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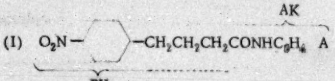
* See Consultants Bureau Translation, page 949.
** See Consultants Bureau Translation, page 347.
*** See Consultants Bureau Translation, pages 491, 499, 667.
**** See Consultants Bureau Translation, page 491.

SEPARATE CHROMOPHORE SYSTEMS

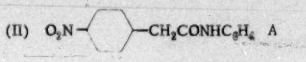
XXVII. COLORABILITY PHENOMENA OF THE ARYL AMIDES OF γ-[4-NITROPHENYL]-BUTYRIC ACID

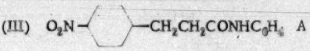
E. A. Smirnov

The aryl amides of γ-[4-nitrophenyl]-butyric acid, under consideration in the present report, correspond to general formula (I), where A is the electron donor (auxochrome) group, OCH_3, OH or $N(CH_3)_2$, located in the para- or meta-position in relation to the NH.



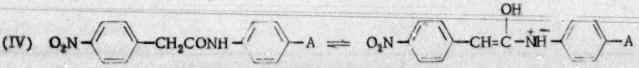
Similarly to the 4-nitrophenylacetic (II) and 4-nitrohydrocinnamic (III) acid derivatives which we synthesized earlier [1], the compounds of the present series should be considered as compounds with separate chromophore systems, i.e., such compounds, for which the electron donor* system AK and the electronophilic** system BK are not conjugate to each other.

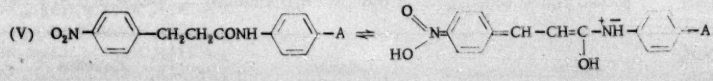




The presence of three CH_2-groups in the nitrophenylbutyric acid derivatives excludes any possibility of formation of a continuous conjugated chain between these systems, even on the assumption of the possibility of tautomeric transformations.

For derivatives of nitrophenylacetic and to a known extent for nitrohydrocinnamic acid (V) derivatives also, a similar possibility is not completely excluded, although it is also extremely unlikely for the latter.





The same also excludes the possibility of accounting for the colorability phenomenon for the nitrophenylbutyric acid derivatives from the point of view of conjugation theory [2].

Introduction of a third CH_2-group in the molecule is interesting also in another respect, namely, it enables us to a known degree to solve the problem of where one should look for the source of the deeper color of the p-nitrohydrocinnamic acid (III) derivatives as compared with the color of the p-nitrophenylacetic acid (II) derivatives – to the elongation of the small chain of carbon atoms and to the weighting molecules connecting to them, or to the possibility of a transferral of the effects between the CO and NO_2-groups by means of an alternation of the polarization (such a proposal was expressed by V. A. Izmailsky and E. A. Smirnov [1]).

Visual observations and reflection spectra. As is evident from Table 1, the first representatives of the present series of compounds (No. 1 and 2), which contain the weakest electron donor group, OCH_3, are colorless. For

* An electron donor system is a conjugated system of double bonds with an electron donor group joined to them.
** An electronophilic system is a conjugated system of double bonds with an electronophilic group joined to them.

compounds with the OH-group a visible color appears, but is still weakly expressed; the compound with a m-OH group (No. 3) was tinted a pale, greenish-yellow color, and the compound with a p-OH group was almost colorless. However, compounds which contain the strongest electron donor group, $N(CH_3)_2$, have a rather deep color: orangish-yellow in the presence of the m-$N(CH_3)_2$ group (No. 5), and yellow-orange in the presence of the p-$N(CH_3)_2$ group (No. 6). Table 2 enables us to compare the visual color of the nitrophenylbutyric acid derivatives with that of the corresponding nitrophenylacetic and nitrohydrocinnamic acid derivatives.*

TABLE 1

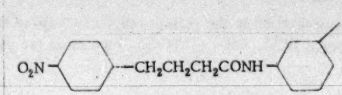
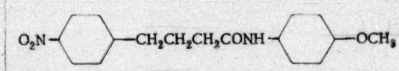
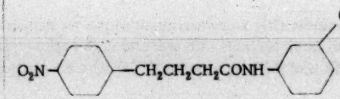
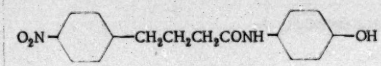
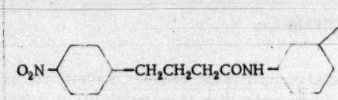
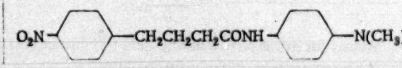
No.	Formulas of compounds	Color of substance in crystals	Color of substance in powder
1			
2		colorless	colorless
3		pale greenish yellow	almost colorless
4		almost colorless	colorless
5		orangish-yellow	orangish-yellow
6		yellowish-orange	orangish-yellow

TABLE 2

No.	Substitution of donor group A	Color of compounds (in powder)		
		p-$O_2NC_6H_4CH_2CONHC_6H_4$ A	p-$O_2NC_6H_4(CH_2)_2CONHC_6H_4$ A	p-$O_2NC_6H_4(CH_2)_3CONHC_6H_4$ A
1	m-OCH_3	Colorless	Colorless	Colorless
2	p-OCH_3			
3	m-OH	Pale yellowish	Pale yellow	Almost colorless
4	p-OH	Almost colorless	Light yellow	Colorless
5	m-$N(CH_3)_2$	Orangish-yellow	Yellow-orange	Orangish-yellow
6	p-$N(CH_3)_2$	Yellow-orange	Yellowish-orange	Orange-yellow

It is evident from Table 2 that all the nitrophenylbutyric acid derivatives which have a visible color are somewhat more deeply colored than are the corresponding nitrohydrocinnamic acid derivatives. It is easily possible to observe this difference for both compounds with OH-group, which have in the nitrohydrocinnamic acid series pale-yellow and light-yellow colors, and in the nitrophenylbutyric acid series are almost colorless, as well as in compounds with the $N(CH_3)_2$-group, in the first case colored a yellow-orange and in the second, only an orange yellow color.

* In order to eliminate the influence of the size of the crystals on the color, the substances for comparison were used as fine powders.

Thus, if on transition from the nitrophenylacetic acid derivatives to the nitrohydrocinnamic acid derivatives, i.e., on introduction of a second CH_2-group into the connecting member, a deepening of the color is observed, then on transition from the latter to the nitrophenylbutyric acid derivatives, i.e., on introduction of a third CH_2-group, we observe, on the other hand, an increase of the color, and consequently, the nitrophenylbutyric acid derivatives show more similarity in their color to the nitrophenylacetic than to the nitrohydrocinnamic acid derivatives.

A comparison of the color of the nitrophenylbutyric acid derivatives with that of the corresponding nitrophenylacetic acid derivatives showed that, for the former a certain tendency toward an increase of the color was observed, as compared with the latter.

The indicated regularities, established on the basis of visual observations, were confirmed by reflection curves obtained for the substances in the solid form (as a powder) and are represented in Figs. 1 and 2.* In all cases the reflection curves of the nitrohydrocinnamic acid derivatives were inclined toward the right more than were those of

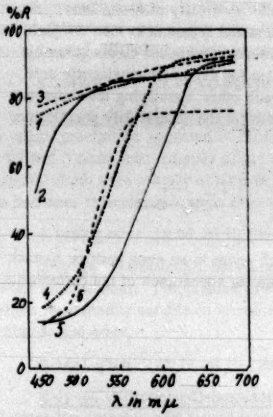


Fig. 1. Reflection curves.
1) p-$O_2NC_6H_4CH_2CONHC_6H_4OH$-p,
2) p-$O_2NC_6H_4(CH_2)_2CONHC_6H_4OH$-p,
3) p-$O_2NC_6H_4(CH_2)_3CONHC_6H_4OH$-p,
4) p-$O_2NC_6H_4CH_2CONHC_6H_4N(CH_3)_2$-p,
5) p-$O_2NC_6H_4(CH_2)_2CONHC_6H_4N(CH_3)_2$-p,
6) p-$O_2NC_6H_4(CH_2)_3CONHC_6H_4N(CH_3)_2$-p.

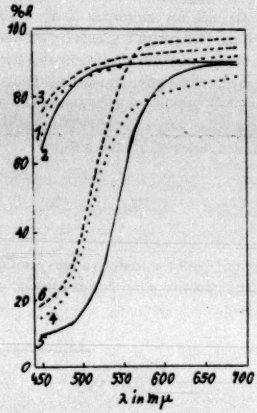


Fig. 2. Reflection curves.
1) p-$O_2NC_6H_4CH_2CONHC_6H_4OH$-m,
2) p-$O_2NC_6H_4(CH_2)_2CONHC_6H_4OH$-m,
3) p-$O_2NC_6H_4(CH_2)_3CONHC_6H_4OH$-m,
4) p-$O_2HC_6H_4CH_2CONHC_6H_4N(CH_3)_2$-m,
5) p-$O_2NC_6H_4(CH_2)_2CONHC_6H_4N(CH_3)_2$-m,
6) p-$O_2NC_6H_4(CH_2)_3CONHC_6H_4N(CH_3)_2$-m.

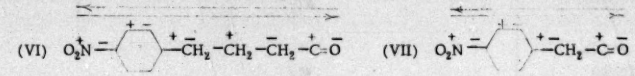
the corresponding nitrophenylacetic and nitrophenylbutyric acid derivatives, i.e., were shifted toward the longer waver, which corresponds to the deeper color of these compounds. On the other hand, the reflection curves of the nitrophenylbutyric acid derivatives were found to have the most hypsochromic arrangements, which in the present case, again corresponded to the deep color of these compounds, as compared with the color of the analogous compounds of the two other series.

In connection with the fact that, for the nitrophenylbutyric acid derivatives, as has already been observed above, neither tautomeric transformations no electronic displacements can lead to formation of a continuous continuous conjugated chain in the molecule which would be the conductor of the effect between the NO_2 and the

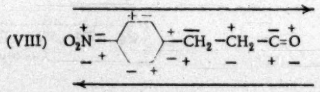
* % R is the percent of monochromatic light reflected by the present compounds in comparison with the amount of the same light reflected by magnesium oxide (a more detailed description of the obtainment of the reflection curves was given in a preceding report [3]).

electron donor groups, it must be postulated that the only route by which an interaction can occur between the electronophilic and electron systems would be their direct interaction with the help of the external field forces, "exomolecular forces" [4], i.e., forces which, in the case of the interaction of two different molecules containing systems (electronophilic and electron donor) of opposing character, would lead to the formation of intensely colored complex compounds. This interaction also is the basic factor which specifies the color of the compounds being considered. The great similarity of their colors with the color of the analogous nitrophenylacetic and nitrohydrocinnamic acid derivatives indicated also that in the last two series of compounds the fundamental reason for the colorability is the same, i.e., direct interaction of two oppositely-polarized chromophore systems. This conclusion, made on the basis of visual observations and supported by reflection spectra measurements, finds further confirmation in the study of the absorption spectra of the three series of compounds indicated.

For an explanation of the deeper color of the p-nitrohydrocinnamic acid derivatives as compared with the color of the corresponding p-nitrophenylacetic acid derivatives, as already mentioned above, an assumption was expressed [1], according to which one should look for the reason for this either in the elongation of the little chain of carbon atoms and the weighting molecules connected with them, or in the possibility of the transferral of the effect between the CO and the NO_2 groups by means of an alternation of polarization. A weakening of the phenomenon of colorability, observed on transition from the nitrohydrocinnamic acid derivatives to the nitrophenylbutyric acid derivatives, obviously, militates against the former of the alternate explanations. If the possibility of a transferral of the influences between the CO and NO_2 groups by means of alternation of polarization is assumed, then the presence of the latter should lead to formation of nitrophenylbutyric acid derivatives of relatively weaker chromophore systems than for the nitrohydrocinnamoyl derivatives, because for the former, as also for the nitrophenylacetic acid derivatives, the CO and NO_2 groups occur in an uneven position in relation to each other, specifying the same possibility of corresponding polarizing effects [(VI) and (VII)], which is less favorable for the colorability phenomenon (as was found for an entire series of instances [5]):



For the nitrohydrocinnamic acid derivatives the CO and NO_2 groups, which occur in an even position to each other (VIII), also produce opposite polarization effects, which are more favorable for appearance of the chromophoric properties of the system:



Thus, this point of view enables one to explain the deeper color of the nitrohydrocinnamic acid derivatives as compared with the color of the corresponding derivatives of both nitrophenylacetic and nitrophenylbutyric acids.

EXPERIMENTAL

γ-Phenylbutyric acid was obtained from β-phenylethyl bromide by means of malonic ester, according to literature data [6]

γ-[4-Nitrophenyl]-butyric acid. Nitric acid d 1.5 (35 ml), cooled to 0°, was added to γ-phenylbutyric acid 16.4 g) which was placed in a beaker, and the mixture, cooled externally with ice water, was stirred until disappearance of the crystals was complete. After this the mixture was poured onto ice, and the precipitate which formed at this time was treated several times with hot water (in order to dissolve the possible o-isomer impurity). Then the precipitate was dissolved in acetic acid by heating, and an equal volume of water was added to the resulting solution, after which addition of water was made dropwise until formation of the precipitate was complete. The latter was recrystallized again from water. The substance (9.2 g), obtained as colorless, acicular crystals with a m.p. of 92°, was very readily soluble in ether, benzene, chloroform, carbon tetrachloride and acetic acid, and much more difficultly soluble in water.

0.2347 g sub.: 14.35 ml N_2 (18.5°, 752 mm)*. Found %: N 6.97. $C_{10}H_{11}O_4N$. Calculated %: N 6.70.

The acid chloride of γ-[4-nitrophenyl]-butyric acid was obtained by the action of an equivalent quantity of phosphorus pentachloride on p-nitrophenylbutyric acid. After removal of the phosphorus oxychloride in vacuo, the

* The nitrogen was collected and measured over 30% KOH solution.

acid chloride which remained was dissolved in a small amount of dry benzene, and the benzene solution was used for obtainment of the corresponding aryl amides, for which the acid chloride was taken in a small excess (10% as compared to the theoretical). The condensation with amines was carried out in a water-benzene medium in the presence of sodium bicarbonate, analogously to the production of the aryl amides of p- and m-nitrobenzoic acids described earlier [7].

4-[γ-(4'-Nitrophenyl)-butyramino]-anisole (Table 1, No. 2). Obtained as a result of the reaction of p-anisidine and the acid chloride of p-nitrophenylbutyric acid, the precipitate was recrystallized 2 times from alcohol. The pure product consisted of colorless crystals with a m.p. of 134-5°, was readily soluble in acetone and in chloroform even in the cold, highly soluble in alcohol and in benzene, less soluble in carbon tetrachloride, and difficultly soluble in ether.

0.1758 g sub.: 14.25 ml N_2 (18°, 750 mm). Found %: N 9.23 $C_{17}H_{18}O_4N_2$. Calculated %: N 8.92.

3-[γ-(4'-Nitrophenyl)-butyramino]-anisole (Table 1, No. 1.). The reaction product did not precipitate at once, but only after some time. After separation the precipitate was recrystallized 2 times from dilute alcohol (water was added gradually to the alcoholic solution according to the extent of precipitation of the crystals) and 1 time from methyl alcohol. The resulting colorless, flaky crystals with a m.p. of 97°, were readily soluble in acetone and in chloroform even in the cold, highly soluble in alcohol and in benzene, rather highly soluble in carbon tetrachloride, and difficultly soluble in ether.

0.1449 g sub: 11.65 ml N_2 (19.5°, 749 mm). Found %: N 9.05. $C_{17}H_{18}O_4N_2$. Calculated %: N 8.92.

4-[γ-(4'-Nitrophenyl)-butyramino]-phenol (Table 1, No. 4). On addition of the chloride solution to an amine a yellow precipitate appeared immediately, which on further shaking was decolorized. The precipitate was recrystallized 2 times from slightly dilute (8:1) alcohol. Almost colorless, flaky crystals with a m.p. of 182° were obtained, which were readily soluble in alcohol and in acetone (in the latter even in the cold) and difficultly soluble in benzene, chloroform, carbon tetrachloride and ether.

0.1430 g sub.: 12.06 ml N_2 (20.4°, 744 mm). Found %: N 9.41. $C_{16}H_{16}O_4N_2$. Calculated %: N 9.33.

3-[γ-(4'-Nitrophenyl)-butyramino]-phenol (Table 1, No. 3). The resulting precipitate was recrystallized 2 times from alcohol. The product crystallized as small, pale greenish-yellow, oval tablets, with a m.p. of 177°, which were readily soluble in acetone and in alcohol, and difficultly soluble in benzene, chloroform, carbon tetrachloride and ether.

0.1441 g sub.: 12.19 ml N_2 (19.6°, 742 mm). Found %: N 9.47. $C_{16}H_{16}O_4N_2$. Calculated %: N 9.33.

4-[γ-(4'-Nitrophenyl)-butyramino]-dimethylaniline (Table 1, No. 6). The reaction product was recrystallized 3 times from alcohol and 1 time from benzene (with carbon). The resulting yellow-orange-colored crystals, which had the form of long narrow plates, with a m.p of 153°, were readily soluble in acetone and in chloroform even in the cold, highly soluble in alcohol and in benzene, poorly soluble in carbon tetrachloride, and difficultly soluble in ether.

0.1294 g sub: 14.92 ml N_2 (21.5°, 752 mm) Found %: N 12.97. $C_{18}H_{21}O_3N_3$. Calculated %: N 12.85.

3-[γ-(4'-Nitrophenyl)-butyramino]-dimethylaniline (Table 1, No. 5). On shaking a chloride solution with m-aminodimethylaniline, a voluminous, greenish-yellow precipitate formed which was apparently a combination of the product sought and benzene (precipitate melted very readily and was very readily flammable). After 2 crystallizations from alcohol the product was obtained as long, narrow, orange-yellow-colored tablets with a m.p. of 107°, which were readily soluble in acetone and in chloroform, even in the cold, highly soluble in alcohol and in benzene, rather highly soluble in carbon tetrachloride and much less soluble in ether.

0.1330 g sub.: 15.61 ml N_2 (22.3°, 745 mm). Found %: N 13.05. $C_{18}H_{21}O_3N_3$. Calculated %: N 12.85.

SUMMARY

1. A series of compounds, derivatives of γ-[4-nitrophenyl]-butyric acid of the general formula (I), where A is one of the electron donor (auxochromic) groups OCH_3, OH, $N(CH_3)_2$, located in the meta- or para-position in relation to NH, was synthesized.

2. The compounds which contained an OH or $N(CH_3)_2$ group, have a visible color, which is rather deep in the presence of the latter: orange-yellow for m-$N(CH_3)_2$ and yellow-orange for p-$N(CH_3)_2$.

3. All the compounds of the present series were found to be somewhat less deeply colored than the corresponding 4-nitrohydrocinnamic acid derivatives, and closer in their color to the 4-nitrophenylacetic acid derivatives.

4. Thus, on subsequent transition from the 4-nitrophenylacetic acid derivatives to the corresponding 4-nitrohydrocinnamic derivatives, and further to the γ-[4-nitrophenyl]-butyric acid derivatives, a reversal of color was observed: at first its decrease, and later its increase took place. As a result, the 4-nitrohydrocinnamic acid derivatives showed the deepest colors.

5. Reflection spectra were measured for all the compounds, both of the present series and for the 4-nitrophenylacetic and 4-nitrohydrocinnamic acid derivatives.

6. The order of positions of the reflection curves corresponded to the order of the color changes of the compounds, and consequently, confirmed the validity of the visual observations.

7. The presence of three CH_2-groups in combination of a member of the nitrophenylbutyric acid derivatives excludes the possibility of formation of a continuous conjugated chain between the electronophilic and electron donor chromophore systems of these compounds, and excludes the possibility of explanation of the colorability phenomenon from the point of view of conjugation theory.

8. Thus, only the direct interaction of the electronophilic and electron donor chromophore systems, by means of the force of an external field (according to the type of formation of the complex compounds) seems to be the fundamental factor specifying the color of the compounds of the present series.

9. We should search for the reason for the deeper color of the 4-nitrohydrocinnamic acid derivatives, in comparison with the color of the corresponding 4-nitrophenylacetic and 4-nitrophenylbutyric acid derivatives, in the possibility of a transferral of the effects between CO and NO_2 groups by means of an alternation of the polarization, which stipulates the somewhat stronger chromophoric properties of the electronophilic system of the nitrohydrocinnamic acid derivatives as a result of the presence in them of contra-polarizing effects, most favorable for the phenomenon of colorability.

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INVESTIGATIONS IN THE ANTHRAQUINONE SERIES

XXIII. HYDROLYSIS OF ANTHRAQUINONE-α-SULFO ACID*

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The hydrolytic acition of water on anthraquinone-sulfo acids is somewhat different from that of other sulfo acids of the aromatic series. A series of investigators indicated that the hydrolysis of anthraquinone-sulfo acids by heating with an aqueous solution of sulfuric acid is impossible [1]. In a number of cases the presence of certain substituents in the anthraquinone nucleus facilitates the hydrolysis of the sulfo group. Thus, for example, it is known that the 3,8- and 3,5-disulfo acids of 1,2-dihydroxyanthraquinone, on heating in 70-80% sulfuric acid at 150-180° are hydrolyzed with the splitting off of the sulfo group in the third position of the nucleus [2]. In practice the hydrolysis of anthraquinone-α-sulfo acid to anthraquinone was accomplished in 70-85% sulfuric acid at 170-200° after 8-12 hours, only with the addition of 1-5% of mercury sulfate by weight of the hydrolyzing substance [3].

In 1947 we found that, the literature data notwithstanding, it is possible to carry out the hydrolysis of anthraquinone-α-sulfo acid in 70-85% sulfuric acid, in the absence of mercury, and obtain anthraquinone [4].

Data on the hydrolysis of anthraquinone-α-sulfo acid, in the absence and in the presence of mercuric compounds, are cited in the present paper. We carried out experiments of the hydrolysis of anthraquinone-α-sulfo acid in sealed tubes, i.e., at a constant water or water vapor concentration. 0.72 g of the α-sulfo acid (0.0025 mole) was hydrolyzed with 25 ml of H_2SO_4 at different concentrations of the latter and with different durations.

It is evident from the data of Table 1, A that the hydrolysis of anthraquinone-α-sulfo acid, in 60-86% sulfuric acid at 230° for 6 hours, terminated at 22-59%. Under these same conditions, hydrolysis of the sodium salt of anthraquinone-α-sulfo acid amounted to 81-84%.

It is evident from the data of Table 1, B that the rate of hydrolysis was extremely high, and that the length of time (from 1 to 18 hours), just as for the increase of temperature from 190-230° (Table 1, C), decreased the yield of anthraquinone. This decrease of the anthraquinone yield was a result of the side reaction of sulfonation of anthraquinone, with the formation of anthraquinone-β-sulfo acid which was more stable under these conditions, according to Scheme (I):

$$C_{14}O_2H_7SO_3H\text{-}\alpha + HOH \longrightarrow C_{14}O_2H_8 + H_2SO_4 \longrightarrow C_{14}O_2H_7SO_3H\text{-}\beta + H_2O$$

(I)

The presence of a mixture of anthraquinone-α-sulfo and β-sulfo acids could be determined in the mother liquors from the hydrolysis experiments in 85% sulfuric acid at an elevated temperature (210-230°). Meyer and Lauer [3] observed the secondary sulfonation of anthraquinone, which was formed by hydrolysis of the α-sulfo acid in 85% sulfuric acid at temperatures above 210°, in the presence of mercury.

We detected the sulfonation of anthraquinone at 210-230° by 85-100% sulfuric acid (70% sulfuric acid did not sulfonate under these conditions). Thus, the fundamental characteristic of the behavior of anthraquinone-α-sulfo acid on hydrolysis consists only of its great stability toward hydrolytic cleavage, which proceeds under the more rigorous conditions (high temperature and pressure).

The conditions of hydrolysis of anthraquinone-α-sulfo acid are modified by mercury salts, which enable us to carry out the hydrolysis at lower temperatures (170-190°) in an open system, and also in 5% sulfuric acid at 230°, but in a closed system (Table 2).

The rate of hydrolysis of anthraquinone-α-sulfo acid in the presence of mercury is very high, both in an open and in a closed system. As is evident from the data of Table 3, B, after 15 minutes at 230°, in 70% sulfuric acid with 5% mercury sulfate (by weight of the sulfo acid), the anthraquinone yield amounted to 54%. Hydrolysis proceeded somewhat more slowly in a closed system than in an open system. The hydrolysis did not depend on the nature of the mercuric salts. The latter after hydrolysis, just as in the sulfonation of anthraquinone to the monosulfo acid in the presence of mercury, was distributed between two media: as ionized mercury in the mother sulfuric acid solution, and as a non-ionized combination in the anthraquinone which formed. The increase of the rate of hydrolysis

* XXII. J. Gen. Chem., 25, 565 (1955). (See Consultants Bureau Translation, page 535).

TABLE 1

Hydrolysis of Anthraquinone-α-sulfo Acid in Sulfuric Acid, Without Mercury (0.72 g, 25 ml of H_2SO_4)

Expt. No.	Sulfuric acid concentration (%)	Moles content of water per mole of sulfo acid	Time (in hours)	Temperature	Obtained					
					anthraquinone		chloroanthraquinone		sulfo acid (in %)	
					(g)	(%)	(g)	m.p.	α	β
				A. Effect of concentrated sulfuric acid						
1	100	4.4	6	230°	None	–				
2	85	147.1	6	230	0.3062	58.9				
3	70	193.0	6	230	0.21	40.4				
4	60	327.0	6	230	0.116	22.3				
5	40	433.0	6	230	None	–				
				B. Effect of time						
6	85	147.1	1	230	0.3110	59.8	0.24	159°	40	None
7	85	147.1	3	230	0.3031	58.3	0.248	159	41	None
8	85	147.1	6	230	0.3062	58.9	0.24	159.5	40	Traces
9	85	147.1	12	230	0.2276	43.8	0.339	169	31	25
10	85	147.1	18	230	0.1738	33.4	0.396	175	31	35
				C. Effect of temperature						
11	85	147.1	6	170	None*					
12	85	147.1	6	190.0	0.3348	64.4				
13	85	147.1	6	210	0.3076	59.15**				
14	85	147.1	6	230	0.3062	58.9**				

TABLE 2

Hydrolysis of Anthraquinone-α-sulfo Acid in Sulfuric Acid with Mercury (0.72 g, 6 hours)

Expt. No.	Sulfuric acid concentration (%)	Moles content of water per mole of sulfo acid	Temperature	Quantity of $HgSO_4$		Sulfuric acid (in ml)	Anthraquinone obtained	
				(g)	% of acid		(g)	(%)
				A. Effect of concentrated sulfuric acid				
1	5	546.6	230°	0.036	5	25	0.45	86.5
2	10	533.0	230	0.036	5	25	0.458	88.8
3	20	508.0	230	0.036	5	25	0.44	84.61
4	30	475.0	230	0.036	5	25	0.428	82.3
5	40	433.0	230	0.036	5	25	0.402	77.3
6	60	327.0	230	0.036	5	25	0.4114	79.1
7	70	193.0	230	0.036	5	25	0.448	86.1
8	85	147.1	230	0.036	5	25	0.457	88.0
9	100	4.4	230	0.036	5	25	0.03	5.7
				B. Effect of temperature				
10	85	147.1	170	0.036	5	25	0.0424	8.1
11	85	147.1	190	0.036	5	25	0.335	64.4
12	85	147.1	210	0.036	5	25	0.408	78.0
13	85	147.1	230	0.036	5	25	0.4576	88.0
				C. Significance of quantity of $HgSO_4$				
14	85	147.1	230	0.0072	1	25	0.3100	60.0
15	85	147.1	230	0.036	5	25	0.4576	88.0
16	85	147.1	230	0.090	12.5	25	0.4100	79.0
				D. Significance of volume of sulfuric acid				
17	85	147.1	230	0.036	5	5	0.411	79.0
18	85	147.1	230	0.036	5	25	0.4576	88.0

* The original sulfo acid remained in solution unchanged.

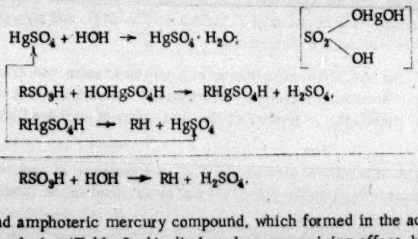
** The presence of anthraquinone-α-sulfo and β-sulfo acids was determined in the solution.

TABLE 3

Mercury Balance for Hydrolysis of Anthraquinone-α-sulfo Acid (0.72 g of the substance; 25 ml of 70% H_2SO_4; 230°; 3.6% catalyst on the basis of HgO by weight of the α-acid)

Expt.	Catalyst		Time (in min.)	Hg found				Sum (%)	Anthraquinone obtained		
	name	quantity (g)		in solution		in anthraquinone			(g)	(%)	HgO content (%)
				(g)	% of that taken	(g)	% of that taken				
				A. Significance of nature of catalyst							
1	$HgSO_4$	0.036	360	0.0137	57.3	0.0092	38.3	95.6	0.448	86.1	2.2
2	Hg_2SO_4	0.0302	360	0.0175	73.0	0.0054	22.5	95.5	0.4396	84.5	1.3
3	$HgCl_2$	0.033	360	0.0199	83.0	0.0031	13.0	96.0	0.4284	82.4	0.7
4	HgCl	0.0286	360	0.0154	64.1	0.0071	30.0	94.1	0.4416	85.0	1.7
5	HgO	0.0263	360	0.0150	57.0	0.0107	40.7	97.7	0.4500	86.5	2.3
6	Hg	0.0243	360	0.0192	73.3	0.0064	24.4	97.7	0.3550	68.2	1.8
				B. Significance of duration							
7		0.036	15	0.0232	96.5	0.0025	10.4	106.9	0.2818	54.2	0.95
8		0.036	30	0.0225	93.7	0.0028	11.6	105.3	0.2942	58.5	0.95
9		0.036	45	0.0225	93.7	0.0025	10.4	104.1	0.3550	68.2	0.76
10	$HgSO_4$	0.036	60	0.0169	70.4	0.0070	29.5	99.9	0.3950	76.0	1.77
11		0.036	180	0.0162	67.3	0.0079	33.0	100.3	0.447	86.0	1.76
12		0.036	360	0.0137	57.3	0.0092	38.3	95.6	0.448	86.1	2.2
13		0.036	540	0.0173	72.0	0.0069	28.0	100.0	0.452	87.0	1.52

of anthraquinone-α-sulfo acid under the influence of mercury, the significance of the quantity of the latter (Table 2, C), and the rapid combination of the mercury with anthraquinone, were a result of the direct interaction of anthraquinone-α-sulfo acid and the hydrated mercury salts in the sulfuric acid medium [6] (Scheme II):



The hydrated and amphoteric mercury compound, which formed in the aqueous solution of sulfuric acid, particularly in the 5-20% solution (Table 2, A), displayed no mercurizing effect, but possessed a capacity for an exchange reaction with the sulfo group due to the active hydroxyl group. With the addition of metallic mercury, an obvious decrease of the rate of hydrolysis of the α-sulfo acid could be observed. The retarded dissolving of mercury in the aqueous sulfuric acid solution also inhibited the hydration of the mercury sulfate which formed, and consequently, also inhibited the reaction of the hydrated mercury with the anthraquinone-sulfo acid. The α-anthraquinonyl-mercury sulfate which formed from the anthraquinone-sulfo acid and the hydrated mercury salts, as was learned earlier [6], hydrolyzed smoothly with the formation of anthraquinone. The nature of the hydrolyses of the α-anthraquinonyl-mercury sulfate and anthraquinone-α-sulfo acid, in the presence of mercury, were entirely identical.

Anthraquinone-α-sulfo acid was not broken down to the monohydrate on heating, which indicated the impossibility of the formation of intermediate α-anthraquinonyl-mercury sulfate in this system, the smooth cleavage of which under similar conditions was established earlier [6]. Anthraquinone, which formed on hydrolysis of anthraquinone-α-sulfo acid, in the presence of mercuric compounds, contained mercury in the bound form (Table 3). Such anthraquinone is also sulfonated by fuming sulfuric acid to the α-sulfo acid, like the so-called "inverted" anthraquinone, which forms during the independent monosulfonation of anthraquinone in the presence of mercuric salts [5].

Thus, the conditions common to the processes of formation of anthraquinone-α-sulfo acid and its hydrolysis, proceeding via the formation of α-anthraquinonyl-mercury sulfate as an intermediate product, are entirely obvious.

EXPERIMENTAL

1. Starting materials. Anthraquinone-α-sulfo acid consisted of bright-yellow needles, with a m.p. of 212°. Found M 288.1, 289. A 99.6% yield of chloroanthraquinone was obtained from it; its m.p. was 161° The sulfuric acid for the hydrolysis was prepared by distillation of the monohydrate or pure sulfuric acid (d 1.84), with saturation with gaseous SO_3, in its turn obtained by a removal from fuming sulfuric acid. Double-distilled water was used for dilution.

2. Procedure of hydrolysis. 1.44 g (0.005 mole) of anthraquinone-α-sulfo acid was introduced into a 50 ml volumetric flask and brought to the mark with sulfuric acid (concentration of the latter from 5 to 30% and from 85 to 100%). 25 ml of this solution was introduced into a tube 250 mm long with a diameter of 20 mm. For the work with the 30-70% sulfuric acid concentration, because of the difficult solubility of anthraquinone-α-sulfo acid in it, a weighed portion of the α-sulfo acid was introduced directly into the tube; the sulfo acid dissolved completely on heating from 150° and above.

The sealed tube was placed in an iron sleeve and heated, almost completely submerged, in an oil bath The heating of the bath to 170-230° was carried out during 1.5-2 hours. The time of heating to 170° was insignificant, since hydrolysis did not occur at the low temperature [3]. On completion of the experiment, the sleeve and tube were cooled in the air. On the next day the tube was opened and the contents were treated as follows:

a) on hydrolysis by acid of about 20% concentration, the contents of the tube were transferred to a funnel for filtration, washing the precipitate from the tube with water. The washed precipitate was transferred to a watch glass and dried at 100-105°.

b) on hydrolysis by acid about a 20% concentration, the contents of the tube were poured into 50-75 ml of water; on separation of the precipitate, its treatment was carried out analogously to (a); in the absence of a precipitate, the solution was used for further treatment with an obligatory additional sample, with greater dilution with water.

c) on hydrolysis in the presence of mercuric compounds, the precipitate was washed on the filter, at first with 2-5% sulfuric acid, and then with water.

The dried reaction product was weighed and its melting point was determined. In all cases the hydrolysis product was insoluble in sodium hydroxide, almost insoluble in alcohol and in ether, and displayed all the properties of anthraquinone. After crystallization from acetic acid it melted at 276-277°, and showed no m.p. depression on melting in a test sample of a mixture with pure anthraquinone.

The anthraquinone, obtained in the hydrolysis experiments with mercuric salts, was analyzed for its mercury content according to Koshkin [8]. From the mother liquors, by an oxidizing chlorination [7], chloroanthraquinone with a m.p. of 157-159° was separated, apparently, a product of the conversion of unaltered anthraquinone-α-sulfo acid.

In the hydrolysis experiments with 85% sulfuric acid at 210-230°, the presence of anthraquinone-α-sulfo and β-sulfo acids (melting point of the chloroanthraquinone 169-175°) was determined in the mother liquor after separation of the anthraquinone.

The experiment of sulfonation of "inverted" anthraquinone. 0.4 g of "inverted" anthraquinone obtained by hydrolysis of anthraquinone-α-sulfo acid at 230° in 70% sulfuric acid, and which contained 2.2% of combined HgO (experiment 1, Table 3, A) and was dried at 120°, was sulfonated by 0.5 g of 26% fuming sulfuric acid (3.5 hours at 135°). After the standard treatment, 0.15 g (38% of the amount taken) of "inverted" anthraquinone was obtained. In solution, 53.6% of anthraquinone-α-sulfo and 4.6% of anthraquinone-α,α'-disulfo acids were obtained.

SUMMARY

1. It was found that anthraquinone-α-sulfo acid has the capacity to be hydrolyzed to anthraquinone at 190-230° in aqueous solutions of sulfuric acid of different concentrations, without mercury, in a closed system under pressure.

2. The hydrated mercury salts were the factor which modified the conditions of hydrolysis of anthraquinone-α-sulfo acid. By the reaction of the former with anthraquinone-α-sulfo acid, α-anthraquinonyl-mercury sulfate formed as the intermediate product, which later was smoothly hydrolyzed to anthraquinone.

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REACTIONS OF DIKETENE

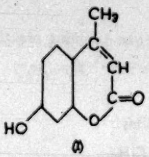
IV. REACTION OF DIKETENE WITH SOME AROMATIC HYDROXYL COMPOUNDS. SYNTHESIS OF METHYLCOUMARIN DERIVATIVES

K. B. Rall and V. V. Perekalin

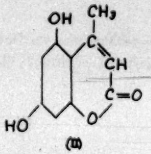
The reaction of diketene with meta-substituted phenols – resorcinol – and triatomic phenols (phloroglucinol, pyrogallol and hydroxyhydroquinone), is essentially different from its reactions with phenol and its ortho- and para-derivatives [1].

In ether, in the presence of traces of concentrated sulfuric acid, resorcinol and diketene at once form 7-hydroxy-4-methylcoumarin (I) (the reaction does not take place without a catalyst), by-passing the acetoacetyl derivative stage.

It was of interest to investigate the effect of a third hydroxyl group on the nature of the reaction of phenols with diketene. The structure of phloroglucinol enabled us to assume that reaction of diketene with it would proceed even more readily than with resorcinol. Actually, in ether in the presence of traces of concentrated sulfuric acid, phloroglucinol and diketene formed a high yield of 4-methyl-5,7-dihydroxycoumarin (II):

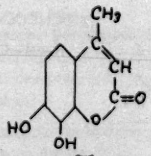


(I)

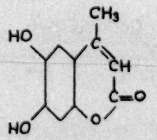


(II)

Pyrogallol may be considered simultaneously as a substituted pyrocatechol and resorcinol; therefore, reaction with diketene may proceed either as with phenol (in that case, if two hydroxyls do not react) or similar to that of resorcinol. Under conditions favorable for the synthesis of acetoacetyl derivatives (in the presence of pyridine), pyrogallol did not react with diketene, but with sulfuric acid in ether, 4-methyl-7,8-dihydroxycoumarin (III) formed; and, finally, 4-methyl-6,7-dihydroxycoumarin (IV) was synthesized from hydroxyhydroquinone in ether, in the presence of sulfuric acid:



(III)

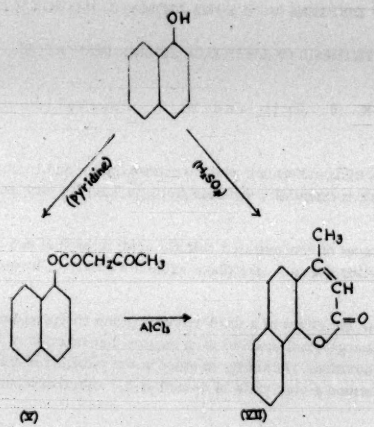


(IV)

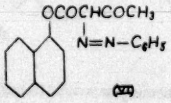
Thus, resorcinol and the triatomic phenols react with diketene, in the presence of sulfuric acid, with the formation of methylhydroxycoumarins. We were unable to synthesize the acetoacetyl derivatives from these phenols.

The hydroxycoumarins did not undergo further acetylation by diketene.

The specificity of the naphthaline molecule was shown by conducting the reaction of 1-naphthol with diketene: in the presence of basic catalysts (pyridine) acetoacetyl-1-naphthol (V) formed, and 4-methyl-7,8-benzocoumarin (VII) was synthesized with acid catalysts. In a nitrobenzene medium, in the presence of aluminum chloride, acetoacetyl-1-naphthol was converted to the product (VII):

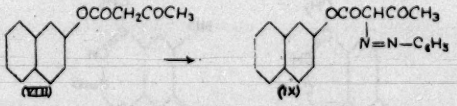


The presence of the acetoacetyl radical was verified by the azo-coupling reaction of product (V) and diazobenzene, forming benzeneazo-acetoacetyl-1-naphthol (VI):



2-Naphthol reacted with diketene only in the presence of pyridine, with the formation of acetoacetyl-2-naphthol (VIII). We were unable to obtain the methylcoumarin derivative from acetoacetyl-2-naphthol or directly from 2-naphthol and diketene.

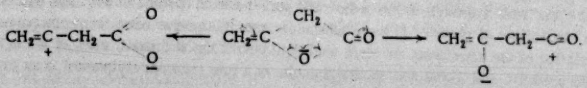
Structure (VIII) was established by synthesis of benzeneazo-acetoacetyl-2-naphthol (IX) from it:



The experimental investigations [1] offer the possibility of proposing a reaction mechanism for diketene and the phenols.

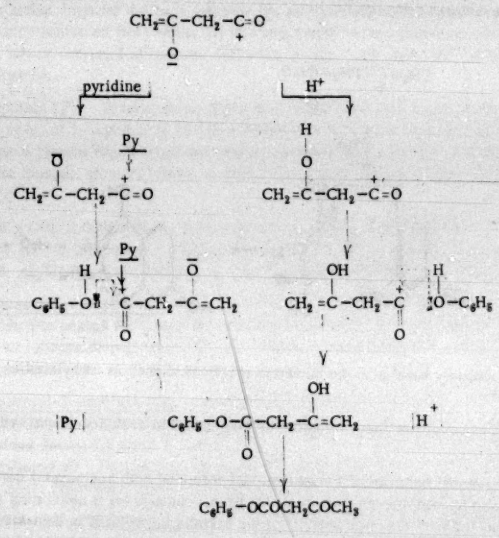
In diketene the unshared pair of electrons of the oxygen of the four-membered heterocycle exists simultaneously in conjugation with the carbonyl group and the vinyl radical. Considering the instability of four-membered heterocycles, particularly the oxygen-containing heterocycles, we could assume that diketene could undergo a

dual polarization, which leads to formation of dipolar molecules more active than the neutral molecules. Polarization would favor substances of both acidic and basic character; their role, apparently, amounts to stabilization of the polarized molecules. The nature of the polarization is determined possibly by the properties of the substance reacting with diketene.



Acetoacetylphenol formed from phenol and diketene only in the presence of basic (pyridine) and acid (sulfuric acid) catalysts which activated diketene

The structure of acetoacetyl derivative indicated that the dipolar diketene molecule with the electron void at the carbonyl carbon atom reacts with phenol; diketene emerges as an acylating agent in the given case, and phenol reacts with it with the unshared pair of electrons of the hydroxyl group. Consequently, the synthesis of the acetoacetylphenols proceeds similarly to the thoroughly studied process of acylation of the amines [2, 3].



(Py = pyridine)

Apparently, the capacity for formation of acetoacetyl derivatives depends on the activity of the unshared pair of electrons of the hydroxyl group. For phenols with acidity constants above 10^{-10}, the activity of the unshared pair of electrons is insufficient for bringing about reaction Literature data on the acylation of aromatic hydroxy compounds are extremely meager; however, it is known that the rate of the benzoylation reaction is inversely proportional to the acidity of the phenol [4].

With few exceptions the ortho-derivatives of phenol do not react with diketene, apparently because of the blocking action of substituents on the hydroxyl.

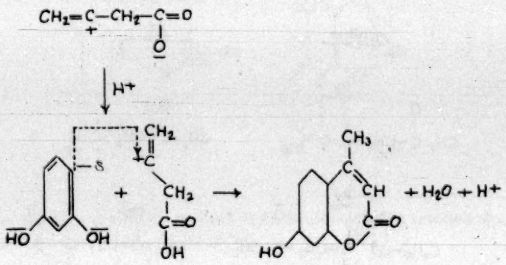
Salicylaldehyde, which occupies a somewhat special position among the ortho-substituted compounds, apparently reacts with diketene as follows: at first the aldehyde carbonyl group and the methylene group of diketene react, and the intermediate compound is converted to 3-acetylcoumarin.

The difficulty of cyclization of the acetoacetyl derivatives (only acetoacetylphenol and acetoacetyl-1-naphthol were converted to coumarin derivatives) probably was connected with the inadequate activation of the ortho-position of the ring and the ease of hydrolysis of the acetoacetyl derivatives.

The mechanism of formation of the coumarin ring reduces to the reaction of the carbonyl carbon (having a diminished electron density) with the carbon atom of the nucleus, followed by elimination of water.

The nature of the reaction of diketene with monatomic phenols in which two hydroxyl groups exist in the meta-position (resorcinol, phloroglucinol, pyrogallol, hydroxyhydroquinone), is entirely different from that of its reactions with diatomic phenols, with hydroxyls in the ortho- and para-position (pyrocatechol and hydroquinone) and other ortho- and para-derivatives of phenol: 1) these substances and diketene at once form compounds of the coumarin series, 2) on variation of the conditions, we were unable to detect the reactions, even of the acetoacetyl derivatives as intermediate products, and 3) the acetoacetylphenols, as a rule (acetoacetylphenol is an exception), did not close the coumarin rings.

In resorcinol, phloroglucinol, pyrogallol and hydroxyquinone the largest electron density will be concentrated in the ortho- and para-positions to the hydroxyl groups. It can be assumed that on formation of the coumarin derivatives the polarized molecule of diketene (with electron void at the vinyl carbon atom) will react with the carbon atom of the nucleus possessing the largest electron density. Then interaction of the reaction centers of the hydroxy compound with diketene leads to formation of a reaction complex, in which a new carbon-carbon bond is established, and the closure of the coumarin ring results.



This synthesis probably belongs to the numerous reactions of phenols carbylated in the ortho-position to the hydroxyl.

Thus, the mechanism of the direct formation of coumarin and acetoacetyl derivatives from diketene and phenols is different.

The somewhat unusual behavior of 1-naphthol, which formed both acetoacetyl derivatives, easily closing the coumarin ring, and also formed directly 4-methyl-7,8-benzocoumarin (as if combining the properties of phenol and resorcinol), was connected with the large activity of the naphthaline nucleus in contrast to that of the benzene nucleus.

EXPERIMENTAL

1. 7-Hydroxy-4-methylcoumarin (I). 5 g (0.059 mole) of diketene, during 10 minutes, was added to a solution of 5.5 g (0.05 mole) of resorcinol in 50 ml of benzene, mixed with several drops of concentrated sulfuric acid, at −10°; the solution was boiled for 2.5 hours. After removal of the ether the vitreous substance was treated with warm acetic anhydride. On cooling the solution crystals of 4-methyl-7-acetohydroxycoumarin (m.p. 151° [5]) were separated, which hydrolyzed on boiling in a 5% solution of hydrochloric acid.

The 7-hydroxy-4-methylcoumarin [5]* consisted of white crystals with a m.p. of 186-187° (from alcohol), was insoluble in water, difficultly soluble in ether and in chloroform, and readily soluble in ethyl alcohol and in acetic anhydride. The yield was 4.8 g (54.5%).

* Structure of (I) and of all the other coumarin derivatives synthesized with the participation of diketene, was established by comparison of their absorption spectra curves and melting points with those of the corresponding coumarins obtained from acetoacetic ester.

2. 5,7-Dihydroxy-4-methylcoumarin (II). Several drops of concentrated sulfuric acid and 1 g (0.012 mole) of diketene were added to a solution of 0.63 g (0 005 mole) of phloroglucinol in 50 ml of ether at −10°. After a 1.5-hour boiling and evaporation of the ether, a yellow precipitate was obtained.

The 5,7-dihydroxy-4-methylcoumarin [6] consisted of lustrous, yellow crystals, with a m.p. of 286-287° (from methyl alcohol), which were insoluble in benzene, chloroform, and ether; they were soluble in methyl and ethyl alcohol on heating. The yield was 0.85 g (88.5%).

3. 7,8-Dihydroxy-4-methylcoumarin (III). Several drops of concentrated sulfuric acid and 2 g (0.024 mole) of diketene were added to a solution of 2 52 g (0.02 mole) of pyrogallol in 25 ml of ether at −10°. After boiling for 1 5 hours and removal of the ether a glassy, resinous substance remained from which, by treatment with alcohol, 7,8-dihydroxy-4-methylcoumarin was separated [6], m.p. 235-236° (from water or concentrated alcoholic solution), which was poorly soluble in water, ether, and benzene, but soluble in alcohol.

4. 6,7-Dihydroxy-4-methylcoumarin (IV). 6.3 g (0.05 mole) of hydroxyhydroquinone was dissolved in 125 ml of ether. The ether solution was cooled and several drops of concentrated sulfuric acid were added to it, and 6 g (0.07 mole) of diketene was added dropwise during 5 minutes; the solution was boiled for 3 hours. After removal of the ether a resinous substance remained from which, by treatment with warm alcohol 6,7-dihydroxy-4-methylcoumarin [7] was separated, which consisted of lustrous, yellowish needles, m.p. 268-269°, which were soluble in water, ether, and acetic anhydride.

5 Acetoacetyl-1-naphthol (V). Several drops of pyridine and 4.5 g (0.053 mole) of diketene were added to a solution of 7.2 g (0.05 mole) of 1-naphthol in 75 ml of benzene at −10°; the solution was boiled for 1.5 hours. After removal of the benzene a viscous liquid remained, which crystallized on cooling. The acetoacetyl-1-naphthol consisted of lustrous, white crystals, m.p. 72° (from alcohol), which were soluble in acetone and in nitrobenzene. The yield was 8.82 g (77.2%).

0.0748 g sub.: 0.2026 g CO_2; 0.0382 g H_2O. 0.0658 g sub.: 0.1785 g CO_2; 0.0334 g H_2O. 0.0843 g sub.: 6.336 g acetone: Δt 0.10°. 0.0866 g sub.: 4.944 g acetone: Δt 0.13°. Found %: C 73.91, 74.03; H 5.71, 5.68. M 222.2, 225.0 $C_{14}H_{12}O_3$. Calculated %: C 73.67; H 5.30. M 228.2.

6. Hydrolysis of the acetoacetyl-1-naphthol. A solution of 0.5 g (0.0022 mole) of acetoacetyl-1-naphthol in 10 ml of 5% sodium hydroxide was heated for 1 hour on a boiling water bath. Acetone was clearly detected in the solution by reaction with o-nitrobenzaldehyde (formation of indigo). After acidification of the solution, 1-naphthol (m.p 94°) was separated quantitatively.

7. Benzeneazo-acetoacetyl-1-naphthol (VI). 2.28 g (0.01 mole) of acetoacetyl-1-naphthol was dissolved in 150 ml of ethyl alcohol and 20 ml of a 0.1 N solution of sodium acetate. 110 ml (0.011 mole) of a 0.1 N solution of diazobenzene was added during 1.5 hours to the solution at −2° and with stirring. After a 2-hour stirring the azo dye which formed was filtered off. The azo dye consisted of lustrous, red crystals, m.p. 112-115° (from alcohol), which were insoluble in benzene, chloroform and acetic anhydride.

0.1135 g sub.: 7.5 ml N_2 (18°, 770.5 mm). 0.1559 g sub.: 11.3 ml N_2 (19°, 767.6 mm). Found %: N 8.72, 8.37. $C_{20}H_{16}O_3N_2$ Calculated %: N 8.43.

8. 4-Methyl-7,8-benzocoumarin (VII). a) From naphthol and diketene. A solution of 7.2 g (0.05 mole) of 1-naphthol in 80 ml of ether at −10° was mixed with several drops of concentrated sulfuric acid and 4.5 g (0.053 mole) of diketene, and boiled for 2.5 hours. After evaporation of the ether from the resin, after treatment with alcohol, 4-methyl-7,8-benzocoumarin [8], m.p. 166-167° (from benzene), separated on heating. The yield was 3.35 g (44.6%).

b) From acetoacetyl-1 naphthol. 0.86 g (0.0065 mole) of anhydrous aluminum chloride was added during 10 minutes to a solution of 1.14 g (0.005 mole) of acetoacetyl-1-naphthol in 10 g of dry nitrobenzene, with stirring. After 48 hours the mixture was heated at 60° for 1 hour, and poured into 75 g of finely-ground ice with 10 ml of 5% hydrochloric acid. The nitrobenzene was driven off with steam, and the reaction substance was treated with ether. After removal of the ether the oily liquid crystallized. The yield of (VII) was 0.85 g (40%).

9. Acetoacetyl-2-naphthol (VIII). 4.5 g (0.058 mole) of diketene was added during 10 minutes, with stirring, to a solution of 7.2 g (0.05 mole) of 2-naphthol in 80 ml of benzene containing several drops of pyridine at −10°. The solution was then boiled for 1.5 hours. After removal of the benzene a viscous liquid remained, which crystallized on cooling.

The acetoacetyl-2-naphthol consisted of lustrous, white crystals, m.p. 82-83° (from alcohol),* which were readily soluble in ether, acetone, chlorobenzene ane chloroform. The yield was 9.08 g (79.6%).

0.0950 g sub.: 0.2565 g CO_2; 0.0486 g H_2O. 0.0964 g sub.: 0.2614 g CO_2; 0.0493 g H_2O. 0.1203 g sub.: 16.085 g benzene: Δt 0.18°. 0.0962 g sub.: 6.444 g acetone· Δt 0.10°. Found %: C 73.69, 73.99; H 5.73, 5.72. M 212.0, 249.2 $C_{14}H_{12}O_3$. Calculated %: C 73.67; H 5.30. M 228.24.

10. Hydrolysis of the acetoacetyl-2-naphthol. A solution of 0.5 g (0.022 mole) of acetoacetyl-2-naphthol in 12 ml of 5% sodium hydroxide was heated for 1 hour on a boiling water bath After evaporation of the solution acetone was detected by reaction with o-nitrobenzaldehyde. 2-Naphthol (m.p. 120°) separated quantitatively on acidification of the solution.

11. Benzeneazo-acetoacetyl-2-naphthol (IX). 40 ml (0.004 mole) of a 0.1 N solution of diazobenzene was added during 1 hour to a solution of 0.8 g (0.0035 mole) of acetoacetyl-2 naphthol in 100 ml of ethyl alcohol, and 20 ml of 0.1 N solution of sodium acetate, cooled to 0°; the benzeneazo-acetoacetyl-2-naphthol consisted of fine, orange crystals, m.p. 132-134° (from alcohol). The yield was 1.1 g (98%).

0.0666 g sub.: 4.8 ml N_2 (18°, 759 mm). 0.1127 g sub.: 8.2 ml N_2 (18°, 770.5 mm). Found %: N 8.27, 8.48. $C_{20}H_{16}O_3N_2$. Calculated %: N 8.43.

SUMMARY

1. A new method was proposed for the synthesis of coumarin derivatives from diketene and aromatic hydroxy compounds.

2. The specific role of acidic and basic catalysts (in the instance of the reaction of 1-naphthol with diketene) was shown: the former favors the synthesis of acetoacetyl derivatives, the latter favors the synthesis of coumarin derivatives.

3. On the basis of assumptions concerning dual polarization of diketene, a mechanism of its reactions with aromatic hydroxyl compounds was proposed, which was different for synthesis of acetoacet 1 and coumarin derivatives.

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* Products (V-VIII), owing to their easy hydrolysis, should be crystallized without bringing the alcoholic solution to boiling.

** See Consultants Bureau Translation, page 259.

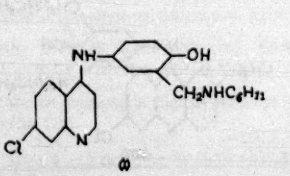
CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

XVII. EFFECT ON ANTIMALARIAL ACTIVITY OF REPLACEMENT OF THE DIETHYLAMINO GROUP IN A LATERAL CYCLIC SUBSTITUENT BY A CYCLIC AMINE (IN COMPOUNDS OF THE QUINOLINE AND ACRIDINE SERIES)

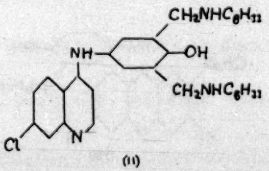
V. I. Stavrovskaya

We reported earlier that the replacement of an aliphatic dialkylaminoalkylamine by substituted m-aminobenzyldiethylamine in compounds of the quinoline and acridine series would involve, together with a decrease of the toxicity of the individual preparations, a considerable increase of their antimalarial activity [1, 2]. This circumstance led us to the idea concerning the possibility of replacement of the diethylamino group in the lateral substituent by a cyclic amine. Such an attempt of replacement of the diethylamino group in aliphatic amines by cyclic nitrogen-containing compounds, in which morpholine, piperidine, and pyrrolidine, chiefly, were used as the nitrogen compounds, was described in the literature [3-7]. In all these cases replacement of the diethylamino group led to a sharp decrease of the activity or to its complete loss. Reitsema and Hunter's work was an exception [8], in which it was reported that the replacement of the diethylamino group in chlorochin by pyrrolidine led to a compound the activity and toxicity of which was similar to that of the same chlorochin.

We used cyclohexylamine and α-methylpyrrolidine as the cyclic amines for replacement of the diethylamino group. 7-Chloro-4(3'-cyclohexylaminomethyl-4'-hydroxyphenyl)-aminoquinoline (I), 7-chloro-4-[3',5'-bis-(cyclohexylaminomethyl)-4'-hydroxyphenyl]-aminoquinoline (II), 2-methoxy-6-chloro-9-[3',5'-bis-(cyclohexylaminomethyl)-4'-hydroxyphenyl]-aminoacridine (III) and 7-chloro-4-[3',5'-bis-(α-methylpyrrolidinomethyl)-4'-hydroxyphenyl]-aminoquinoline (IV) were synthesized, in which the diethylamino group was replaced by α-methylpyrrolidine. The latter was obtained from the monohydrochloride of 1-diethylamino-4-aminopentane by a method which we developed [9].



(I)



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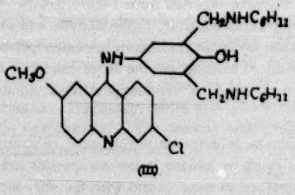
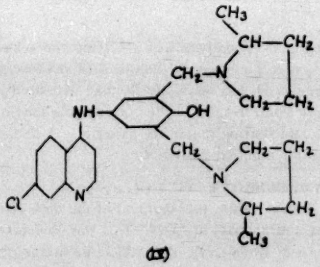


(III)



(IV)

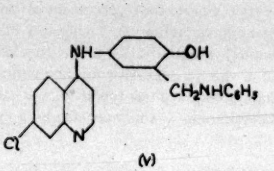
We obtained all the above-described preparations by the Mannich reaction from 7-chloro-4-(4'-hydroxyphenyl)-aminoquinoline or 2-methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine, formaldehyde and the appropriate amine. The mixture of Mannich mono- and dibases which formed was separated on the basis of their different solubilities in ether.

The synthesized compounds showed a high antimalarial activity on testing on P. relictum in greenfinches and linnets. The preparations obtained may be arranged in the following order according to the degree of their effectiveness: substance (IV) was 3-4 times more active than chlorochin and 10 times more active than atabrine; its toxicity was less than that of chlorochin, and close to that of atabrine; substance (II) was approximately 3 times more active than chlorochin, and 8 times more active than atabrine; its toxicity was less than that of chlorochin, and close to that of atabrine; substance (I) was approximately 3 times more active than atabrine; its toxicity was less than that of chlorochin; substance (III) was about 3 times more active than atabrine; its toxicity was considerably below that of atabrine.

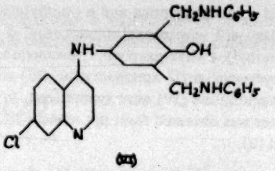
Thus compounds having two cycloaminomethyl groups located in the ortho-position to the hydroxyl and in the meta-position to the NH-group showed the greatest activity, similar to the antimalarial activity of Preparation No. 5 [2].

Furthermore, we replaced cyclohexylamine with aniline, and synthesized the analogous quinoline compounds: 7-chloro-4-(3'-anilinomethyl-4'-hydroxyphenyl)-aminoquinoline (V) and 7-chloro-4-[3',5'-bis-(anilinomethyl)-4'-hydroxyphenyl]-aminoquinoline (VI).

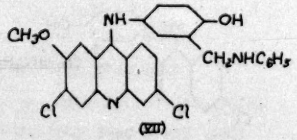
The following acridine compounds were also obtained: 2-methoxy-6-chloro-9-(3'-anilinomethyl-4'-hydroxyphenyl)-aminoacridine (VII), and 2-methoxy-6-chloro-9-[3',5'-bis-(anilinomethyl)-4'-hydroxyphenyl]-aminoacridine (VIII).



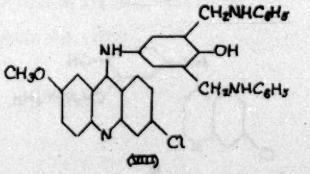
(V)



(VI)



(VII)



(VIII)

We obtained the preparations indicated above by the Mannich reaction from 7-chloro-4-(4'-hydroxyphenyl)-aminoquinoline or 2-methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine, formaldehyde and aniline. The reaction proceeded much less satisfactorily than with diethylamine, cyclohexylamine or α-methylpyrrolidine. The yield was very small in spite of the considerable length of time of heating and the large excess of aniline. About 90% of unreacted starting materials, especially 2-methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine, was recovered from the reaction substance.

Preparations No. (V), (VI), (VII) and (VIII) were found to be inactive on testing on P. relictum in greenfinches and linnets. Thus, replacement of the diethylamino group by aniline in the compounds indicated above destroyed the antimalarial activity. This was obviously connected to some extent with the very weak basicity of the compounds synthesized, which differed sharply from the basicity of all the other quinoline and acridine preparations which we obtained.

We thank Sh. D. Moshkovsky and S. A. Syrkinaya for carrying out the biological tests.

EXPERIMENTAL

7-Chloro-4-[3', 5'-bis-(cyclohexylaminomethyl)-4'-hydroxyphenyl]-aminoquinoline and 7-Chloro-4-(3'-cyclohexylaminomethyl-4'-hydroxyphenyl)-aminoquinoline

7-Chloro-4-(4'-hydroxyphenyl)-aminoquinoline (3.6 g), cyclohexylamine (9.2 g), formalin (3 ml) and alcohol (10 ml) were boiled on the water bath for 11 hours. On completion of the heating the alcohol was removed, the residue consisted of a viscous, cinnamon-colored liquid, it was washed several times with water, then it was dissolved in 10% hydrochloric acid, boiled with carbon, filtered off and alkalized with a potash solution. The yellowish-colored solid product which precipitated was washed with water and dried; 6.5 g was obtained. The well-ground substance was shaken in ether at room temperature, during which a portion of the substance did not go into solution, and was filtered off (1.3 g).

a) The ether solution was dried with potash. After removal of the ether 5 g of a dark, viscous product remained, which was converted to the hydrochloride by dissolving in alcoholic hydrochloric acid. The hydrochloride was precipitated by addition of ether. The orange-colored hydrochloride was purified by dissolving in alcohol followed by addition of ether. On determination of the melting point the following was observed: on slow heating, the substance changed from red-orange to cinnamon-yellow at 160-170°, and did not melt at 270°. With rapid heating it fused at 230°. On determination of the melting point in a sealed capillary the substance melted at 148-150°. It was soluble in water.

3.798 mg sub.: 0.304 ml N_2 (23°, 740 mm). 3.564 mg sub.: 0.284 ml N_2 (24°, 740 mm) Found %: N 8.99, 8.92. $C_{29}H_{41}ON_6Cl_4 \cdot 1.5\ H_2O$. Calculated %: N 8.90.

The base, liberated from the hydrochloride by aqueous ammonia, was crystallized from a mixture of benzene and petroleum ether. It consisted of pale-yellow needles with a m.p. of 118-120°. They were soluble in alcohol, ether and acetone; they were insoluble in water; they were readily soluble in dilute acid, but insoluble in dilute alkali. They gave a cinnamon coloration with ferric chloride.

1.799 mg sub: 0.186 ml N_2 (27°, 752 mm). 2.643 mg sub.: 0.265 ml N_2 (26°, 752 mm). Found %: N 11.64, 11.33. $C_{29}H_{37}ON_4Cl$. Calculated %: N 11.37.

b) The product which did not dissolve in ether (1.3 g) crystallized from alcohol. It consisted of fine needles with a m.p. of 234°. The yellowish-colored base was highly soluble in alcohol and in benzene, poorly soluble in ether, and insoluble in water; it was readily soluble in dilute acids, but insoluble in dilute alkalis. In a water-alcohol solution it gave a cinnamon coloration with ferric chloride.

4.122 mg sub.: 0.402 ml N_2 (21°, 733 mm) 3.916 mg sub.: 0.392 ml N_2 (22°, 740 mm) Found %: N 10.92, 11.28. $C_{22}H_{24}ON_3Cl$. Calculated %: N 11.01.

The hydrochloride consisted of slightly yellowish-colored fine needles with a m.p. of 252°, which corresponded to the literature value [10].

7-Chloro-4-[3', 5'-bis-(α-methyl-pyrrolidinomethyl)-4'-hydroxyphenyl]-aminoquinoline

7-Chloro-4-(4'-hydroxyphenyl)-aminoquinoline (5.4 g), α-methyl-pyrrolidine (7 g), formalin (3.6 ml) and alcohol (30 ml) were boiled on the water bath for 6 hours. All went into solution after 15 minutes of heating. On completion of the heating the alcohol was removed, the residue was dissolved in 10% hydrochloric acid, filtered, alkalized with aqueous ammonia and extracted with ether. The ether solution was washed with water and dried with sodium sulfate. After removal of the ether the residue was again dissolved in 10% hydrochloric acid and alkalized with aqueous ammonia. The curdy, white precipitate which came down was filtered off, washed with water and dried. 6.3 g (66%) was obtained. The product which crystallized from acetone consisted of fine needles, with a m.p. of 186°. The base was soluble in alcohol, benzene, acetone, and dilute acids; it was insoluble in water and in dilute alkalis.

3.548 g sub.: 0.382 ml N_2 (20°, 731 mm). 4.879 mg sub.: 0.529 ml N_2 (21°, 731 mm). Found %: N 12.06, 12.11. $C_{27}H_{33}ON_4Cl$. Calculated %: N 12.06.

The hydrochloride was obtained by passing dry hydrogen chloride into a benzene solution of the base. Its color was yellowish, it was hygroscopic, and its m.p. was 125-127° (decomposition).

For analysis the hydrochloride was brought to constant weight.*

2.552 mg sub.: 0.235 ml N_2 (20°, 753 mm). 3.229 mg sub.: 0.304 ml N_2 (21°, 753 mm). Found %: N 10.63, 10.83. $C_{27}H_{33}ON_4Cl \cdot 2HCl$. Calculated %: N 10.42.

2-Methoxy-6-chloro-9-[3', 5'-bis-(cyclohexylaminomethyl)-4'-hydroxyphenyl]-aminoacridine

2-Methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine (5.2 g), cyclohexylamine (5.4 g), formalin (3 ml) and alcohol (50 ml) were refluxed in a small flask for 11 hours on a boiling water bath, with stirring. On completion of the heating the dark-red liquid was filtered off from the precipitate (1.6 g of the starting material), the alcohol was removed, the remaining viscous substance was washed several times with water and then was extracted with ether. After removal of the ether 7.2 g of a viscous, dark-red liquid remained, which on treatment with 10% hydrochloric acid was converted to the red, solid hydrochloride. The latter was converted to the base by aqueous ammonia, and was extracted with ether; moreover, a portion of the substance did not go into solution.

Such a purification by conversion of the base to the hydrochloride and back, followed by extraction with ether, was repeated several times, which enabled us to separate the Mannich monobase from the dibase, which was found to be 4.7 g. A current of dry hydrogen chloride was passed into an ether solution of the latter. The yellow-orange colored hydrochloride which precipitated was soluble in water and in alcohol. It melted at 215-225° with gradual decomposition.

The hydrochloride was brought to constant weight for analysis.

6.816 mg sub.: 0.509 ml N_2 (21°, 737 mm). 6.819 mg sub.: 0.480 ml N_2 (20°, 746 mm). Found %: N 8.41, 8.05. $C_{34}H_{41}O_2N_4Cl \cdot 3HCl$. Calculated %: N 8.21.

The base was liberated from the hydrochloride by treatment with aqueous ammonia. It was crystallized from benzene. During determination of the melting point it decomposed at about 130°.

2.939 mg sub.: 0.245 ml N_2 (18°, 749 mm) 3.062 mg sub.: 0.255 ml N_2 (20°, 749 mm). Found %: N 9.64, 9.56. $C_{34}H_{41}O_2N_4Cl$. Calculated %: N 9.78.

7-Chloro-4-[3', 5'-di(anilinomethyl)-4'-hydroxyphenyl]- and 7-Chloro-4-(3'-anilinomethyl-4'-hydroxyphenyl)-aminoquinoline

A mixture of 7-chloro-4-(4'-hydroxyphenyl)-aminoquinoline (5.4 g), aniline (18 g), formalin (5 ml) and alcohol (30 ml) were boiled for 13 hours. The alcohol was removed, the residue was alkalized with a 10% solution of sodium hydroxide and extracted with ether in order to remove the unreacted aniline (12.8 g of aniline remained after removal of the ether). The viscous, gummy substance, which did not dissolve in ether, dissolved in 10% hydrochloric acid, and the liquid was filtered off from the insoluble yellowish product (1.4 g), with a m.p. of 253-254°, a test sample of a mixture of which with the original 7-chloro-2-(4'-hydroxyphenyl)-aminoquinoline gave no m.p. depression.

The acid solution was boiled with carbon, alkalized with aqueous ammonia and extracted with ether. A portion of the substance did not dissolve in the ether solution, and was filtered off (1.8 g)

a) The ether solution was washed with water and dried with potash. After removal of the ether 4 g of a gummy substance remained which was treated with alcoholic HCl, followed by addition of ether. The resulting hydrochloride was purified by dissolving it in methyl alcohol and adding ether. Its color was bright yellow, its m.p. was 205-207° (decomposition), and it was poorly soluble in water, with partial hydrolysis of the product.

7.334 mg sub.: 0.529 ml N_2 (20°, 749 mm). 7.878 mg sub.: 0.588 ml N_2 (20°, 748 mm). Found %: N 8.28, 8.58. $C_{29}H_{28}ON_4Cl_4 \cdot 4H_2O$. Calculated %: N 8.46.

The base obtained from the hydrochloride by treatment with aqueous ammonia was a pale yellowish-colored, gummy substance.

3.747 mg sub.: 0.382 ml N_2 (21°, 751 mm). 3.889 mg sub.: 0.402 ml N_2 (21°, 751 mm). Found %: N 11.70, 11.86. $C_{29}H_{25}ON_4Cl$ Calculated %: N 11.65.

* Obviously, on bringing the hydrochloride to constant weight, the loss of one molecule of HCl also occurred; therefore, analyses of the substance correspond to the dihydrochloride, and not to the trihydrochloride. On drying the hydrochloride, the weight of the latter approached constancy; unexpectedly, with a very small increase of the drying chamber temperature a considerable decrease in weight was again observed, which was soon stopped.

b) The product which did not dissolve in ether (1.8 g), dissolved on heating in 10% hydrochloric acid. The hydrochloric acid solution was boiled with carbon, filtered off and alkalized with aqueous ammonia. The base which precipitated was purified by repeated reprecipitation from acid solution, since on attempt to crystallize the substance it precipitated as gummy flocs. The base had a slightly yellowish color, was insoluble in water and in petroleum ether, and was poorly soluble in alcohol, ether and acetone; it was soluble idn benzene, nitrobenzene and in xylene; it was soluble in 10% hydrochloric acid on heating, but was insoluble in dilute alkalis. It gave a cinnamon coloration with ferric chloride. It melted indefinitely at 124-127° with gradual decomposition

5.129 mg sub.: 0.490 ml N_2 (21°, 757 mm). 5.138 mg sub.: 0.392 ml N_2 (21°, 757 mm). Found %: N 11.05, 10.96. $C_{22}H_{18}ON_3Cl$. Calculated %: N 11.18.

The hydrochloride had a yellow color, and was poorly soluble in water, with partial hydrolysis. The m.p. was 105-110° (decomposition)

6.940 mg sub.: 0.529 ml N_2 (21°, 749 mm). 7.040 mg sub.: 0.529 ml N_2 (20°, 749 mm). Found %: N 8.72, 8.63. $C_{22}H_{20}ON_3Cl_3 \cdot 3H_2O$. Calculated %: N 8.36.

2-Methoxy-6-chloro-9-[3',5'-bis-(anilinomethyl)-4-hydroxyphenyl]-aminoacridine and 2-Methoxy-6-chloro-9-(3'-anilinomethyl-4'-hydroxyphenyl)-aminoacridine

2-Methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine (17.5 g), aniline (65 g), formalin (10.5 ml) and alcohol (250 ml) were heated on a boiling water bath for 13 hours. On completion of the heating the solution was filtered off from the yellow precipitate of the 2-methoxy-6-chloro-9-(4'-hydroxyphenyl)-aminoacridine (13 g) which did not react. The alcohol was removed from the filtrate, and the remaining dark-red, viscous liquid was steam-distilled in order to remove the aniline. 10% hydrochloric acid was added to the residue in the flask for production of the hydrochloride. The latter was filtered off, treated with aqueous ammonia and extracted with ether; moreover, a portion of the substance did not go into solution. The ether solution was washed with water and dried with potash. After removal of the ether a viscous, red liquid remained, which again was subjected to the above-described operations of conversion to the hydrochloride, then from it to the base, with extraction of the latter with ether. In this case a portion of the substance was insoluble in the ether solution. This operation was carried out three times in order to separate the substance which was difficultly soluble in ether from that which was readily soluble.

a) The product which was poorly soluble in ether was converted to the hydrochloride by treatment of the base with 10% hydrochloric acid. It was crystallized from alcohol, and its color was dark-yellow. Its m.p. was 255-258°. It was poorly soluble in water.

The hydrochloride of 2-methoxy-6-chloro-9-(3'-anilinomethyl-4'-hydroxyphenyl)-aminoacridine was brought to constant weight for analysis.

3.479 mg sub.: 0.245 ml N_2 (22°, 763 mm). 4.883 mg sub.: 0.353 ml N_2 (21°, 759 mm). Found %: N 8.18, 8.38. $C_{27}H_{24}O_2N_3Cl_3$. Calculated %: N 7.95.

The base obtained from the hydrochloride by treatment with aqueous ammonia was crystallized from benzene. Its color was bright-yellow, and its m.p. was 183-184°. It was highly soluble in benzene and in alcohol, poorly soluble in 10% hydrochloric acid, and insoluble in water and in dilute alkalis.

4.470 mg sub.: 0.353 ml N_2 (20°, 763 mm). 5.567 mg sub.: 0.451 ml N_2 (22°, 752 mm). Found %: N 9.24, 9.28. $C_{27}H_{22}O_2N_3Cl$. Calculated %: N 9.22.

b) The ether solution was washed with water and dried with potash. After removal of the ether a very viscous, yellow liquid remained; the latter was converted to the hydrochloride by treatment with alcoholic HCl, followed by addition of dry ether. The hydrochloride had a yellow color, was purified by dissolving in alcohol and precipitation with ether, and its m.p. was 205-208° (decomposition). It was soluble in water.

4.449 mg sub.: 0.323 ml N_2 (22°, 755 mm). 5.571 mg sub.: 0.402 ml N_2 (22°, 756 mm). Found %: N 8.34, 8.31. $C_{34}H_{29}O_2N_4Cl \cdot 3HCl \cdot H_2O$. Calculated %: N 8.14.

The base, liberated from the hydrochloride by treatment with aqueous ammonia, was a viscous, not very mobile, yellowish substance.

SUMMARY

1. A series of quinoline and acridine compounds, in which the diethylamino group was replaced by cyclohexylamine, α-methylpyrrolidine or aniline, was synthesized and characterized.

2. Replacement of the diethylamino group in the cyclic lateral substituent by cyclohexylamine or α-methylpyrrolidine led to highly active antimalarial compounds.

3. Introduction of aniline instead of the diethylamino group destroyed the antimalarial action.

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* See Consultants Bureau Translation, page 177.

** See Consultants Bureau Translation, page 313.

*** Evidently a typographical error occurs in this reference, as no paper by Stavrovskaya appeared in the issue indicated. Publisher.

ORGANIC INSECTOFUNGICIDES

XVII. SYNTHESIS OF AMIDES AND HYDRAZIDES OF DIALKOXYTHIOPHOSPHORIC ACIDS

N. N. Melnikov and A. G. Zenkevich

The organic compounds of phosphorus are all finding greater and greater application in agriculture as agents for the protection of plants [1-3]. Together with the esters of thiophosphoric and dithiophosphoric acids, the amides of phosphoric and pyrophosphoric acids, which are extremely active systemic insecticides and acaricides, recently began to be used in agriculture [4-7]. Of this group of substances, the octamethyl tetramide of pyrophosphoric acid, which under different trade names (OTPA, Shradan, etc.), was used as a systemic insecticide, is of greatest interest [8, 9]. A series of amides of alkoxyphosphoric acids which, however, proved to be relatively inactive, studied as insecticides [10]. In this respect the amides of the corresponding thiophosphoric acids have been very little studied, unless several patents which appeared recently are considered, but by analogy with the mixed esters of thiophosphoric acid these compounds should possess insecticidal activity, and should have the capacity for acting through the vascular system of plants.

In connection with our statements, the synthesis of a large group of amides of the dialkoxythiophosphoric acids of the general formulas (I) and (II) was undertaken.

$(RO)_2PSNH_2$ (I) $(RO)_2PSN(R')_2$ (II)

The compounds which we obtained, and their properties, are cited in Table 1. The synthesis of these compounds was carried out starting from the dialkylchlorothiophosphates, and ammonia or amines:

$$(RO)_2PSCl + (R')_2NH \longrightarrow (RO)_2PSN(R')_2 + HCl.$$

The hydrazides of the dialkoxythiophosphoric acids with the general formulas (III) and (IV) were synthesized by an analogous method, by the reaction of dialkylchlorothiophosphates with hydrazine hydrate or phenylhydrazine.

$(RO)_2PSNHNH_2$ (III) $(RO)_2PSNHNHC_6H_5$ (IV)

The resulting hydrazides and their properties are cited in Table 2.

The testing of the amides of the dialkoxythiophosphoric acids on granary curculionidae showed that these compounds possess a very low contact insecticidal action, and are not of practical interest in the given direction. The testing of the amides of dialkoxythiophosphoric acids as systemically-acting insecticides showed that only compou with the general formula (I), and the dimethyl- and diethylamides of dimethoxythiophosphoric acid, possess the properties of systemic insecticides. However, because of relatively rapid hydrolysis, the duration of their action is not great, and in the strength of their action they take second place to the octamethyl tetramide of pyrophosphoric acid. In our opinion the establishment of the presence of systemic action in the given group of thiophosphoric acid derivatives is of considerable interest

EXPERIMENTAL

We carried out the preparation of the amides and hydrazides of the dialkoxythiophosphoric acids under the following conditions: an amine or hydrazine was added to a solution of the dialkylchlorothiophosphate in a suitable organic solvent, with cooling and stirring. In the case of ammonia and gaseous amines, the latter were passed through a solution of the dialkylchlorothiophosphate On completion of the reaction, the amine hydrochloride salt which separated was filtered off, the solvent was removed, and the residue was vacuum fractionated. In some cases, in order to remove the amine or hydrazine salt more completely, the reaction mixture was washed with water, the solution of the amide or hydrazide was dried with sodium sulfate, and after removal of the solvent the residue was vacuum distilled. On obtainment of the alkylaryl amides of the dialkoxythiophosphoric acids, treatment of the

TABLE 1

Properties of the Amides of Dialkoxythiophosphoric Acids

Formula	B.p. under pressure (mm)	d_4^{20}	n_D^{20}	P (in %)		S (in %)	
				calculated	found	calculated	found
$(CH_3O)_2PSNH_2$	105-108° (10)	1.2649	1.4982	21.98	21.8 21.8	22.68	22.46 23.15
$(C_2H_5O)_2PSNH_2$	112-115 (9)	1.1456	1.4828	18.34	18.05 18.18	18.93	19.35 18.73
$(C_3H_7O)_2PSNH_2$	82 (0.3)	1.0883	1.4798	15.74	15.99 15.78	16.24	15.71 15.9
$(iso\text{-}C_3H_7O)_2PSNH_2$	82 (0.025)	1.0563	1.4670	15.74	15.28 15.29	16.24	15.5 15.4
$(C_4H_9O)_2PSNH_2$	93-96 (0.1)	1.0407	1.4715	13.76	13.78 14.1	14.25	13.7
$(CH_3O)_2PSN(CH_3)_2$	77-78 (9)	1.1712	1.4766	18.34	18.75 18.8	18.93	19.4 18.7
$(C_2H_5O)_2PSN(CH_3)_2$	97-100 (3)	1.0622	1.4635	–	–	–	–
$(C_3H_7O)_2PSN(CH_3)_2$	79-82 (0.36)	1.0222	1.4640	13.76	13.43 13.27	14.25	14.1 14.2
$(iso\text{-}C_3H_7O)_2PSN(CH_3)_2$	71 (0.6)	1.0070	1.4585	13.76	13.32 13.3	14.25	13.8 14.0
$(C_4H_9O)_2PSN(CH_3)_2$	132 (9)	0.9958	1.4622	12.25	12.12 12.27	12.67	12.7 13.0
$(CH_3O)_2PSN(C_2H_5)_2$	88-91 (9)	1.0905	1.4780	15.74	15.65	16.25	16.6
$(C_3H_7O)_2PSN(C_2H_5)_2$	81-82 (0.45)	1.0029	1.4628	12.25	12.7 12.74	12.67	12.4 12.3
$(iso\text{-}C_3H_7O)_2PSN(C_2H_5)_2$	100 (0.9)	1.0210	1.4620	12.25	11.95 11.78	12.67	12.4 12.2
$(C_4H_9O)_2PSN(C_2H_5)_2$	91-93 (0.3)	0.9799	1.4610	11.03	11.45 11.50	11.38	11.1 11.1
$(CH_3O)_2PSN(C_3H_5)(C_2H_5)$	87-93 (0.05)	1.1904	1.5565	12.61	12.76 12.57	13.08	12.5 12.4
$(C_2H_5O)_2PSN(C_3H_5)(C_2H_5)$	99-107 (0.7)	1.1378	1.5499	11.35	11.14 10.96		
$(C_3H_7O)_2PSN(C_3H_5)(C_2H_5)$	104-108 (0.01)	1.0864	1.5272	10.29	10.60 10.60	10.65	10.47 10.50
$(iso\text{-}C_3H_7O)_2PSN(C_3H_5)(C_2H_5)$	81 (m.p.)	–	–	10.29	10.60 10.67	10.65	10.48 10.35
$(C_4H_9O)_2PSN(C_3H_5)(C_2H_5)$	115 (0.025)	1.0697	1.5245	9.41	9.37 9.82	9.74	9.88 9.64
$(CH_3O)_2PSN(CH_2CH_2OH)_2$	136 (0.15)	1.2470	1.5090	13.52	13.86 13.49	14.00	14.10 14.17
$(C_2H_5O)_2PSN(CH_2CH_2OH)_2$	143-145 (0.035)	1.1742	1.4945	12.05	12.67 12.15	12.47	12.36 12.41
$(C_3H_7O)_2PSN(CH_2CH_2OH)_2$	149-151 (0.03)	1.1313	1.4900	10.86	10.71 10.73	11.20	11.41
$(iso\text{-}C_3H_7O)_2PSN(CH_2CH_2OH)_2$	103-110 (0.05)	1.1292	1.4820	10.86	11.15 11.01		
$(C_4H_9O)_2PSN(CH_2CH_2OH)_2$	156-163 (0.05)	1.0916	1.4850	9.89	10.15 10.25	10.23	9.72 9.65

TABLE 2

Properties of Hydrazides of Dialkoxythiophosphoric Acids

Formula	M.p. or b.p. under pressure (mm)	P (in %)		Comment
		calculated	found	
$(CH_3O)_2PSNHNH_2$	103-109°	19.92	19.91, 19.76	
$(C_2H_5O)_2PSNHNH_2$	83-86	16.83	17.30, 17.40	
$(C_3H_7O)_2PSNHNH_2$	76-80 (0.04 mm)	14.61	14.48	d_4^{20} 1.1031, n_D^{20} 1.4896
$(iso\text{-}C_3H_7O)_2PSNHNH_2$	123-129	14.61	14.50, 14.99	
$(C_4H_9O)_2PSNHNH_2$	110-115 (0.04 mm)	12.90, 12.80	12.70, 12.80	d_4^{20} 1.0598, n_D^{20} 1.5410
$(CH_3O)_2PSNHNHC_6H_5$	83-85	13.33	13.20, 12.90	
$(C_2H_5O)_2PSNHNHC_6H_5$	62-65	11.91	11.78, 11.71	
$(C_3H_7O)_2PSNHNHC_6H_5$	57-62	10.75	10.70, 10.90	
$(iso\text{-}C_3H_7O)_2PSNHNHC_6H_5$	42-45	10.75	11.01, 10.85	
$(C_4H_9O)_2PSNHNHC_6H_5$	19-21	9.70	9.76, 10.32	

reaction mixture was carried out as follows: after completion of the reaction, the solvent was removed, and the residue was washed with water and dissolved in benzene. The benzene solution was dried with anhydrous sodium sulfate, the benzene was removed, and the residue was vacuum distilled.

SUMMARY

For the purpose of study of their insecticidal properties, a series of amides and hydrazides of dialkoxythiophosphoric acids with the general formulas (I), (II), (III), and (IV), which were not described in the literature, were synthesized. Compounds with the general formula (I) possessed the properties of systemic insecticides, but in strength and duration of action they took second place to the octamethyl tetramide of pyrophosphoric acid.

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INVESTIGATION OF THE ALKALOIDS FROM LARGE-LEAF RAGWEED

(Senecio macrophyllus)

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Large-leaf ragweed was collected by P. S. Masagetov in the bottom land of the White River in the North Caucasus in August of 1953. The above-ground part of the plant which was collected was blooming. The alkaloids were extracted from the plants, first moistened with aqueous ammonia, by dichloroethane. The total alkaloid contents in the plants amounted to 0.14%.

The total alkaloids, obtained after removal of the solvent, consisted of a dark, viscous, non-crystalline substance which formed greasy salts with flavianic and perchloric acids, and which did not form a crystalline picrate, picrolonate, hydrobromide, hydrochloride, phosphate or oxalate. The crystalline bitartrate, of composition $C_{13}H_{21}O_3N \cdot C_4H_6O_4$, with a m.p. of 162-164°, $[\alpha]_D^{20}$ +52.3° (c 1.3, H_2O), which was readily soluble in water, and poorly soluble in alcohol, was obtained with an alcoholic solution of tartaric acid. The crystalline, faintly colored base was separated from the tartrate, and it was readily soluble in acetone, alcohol, petroleum ether and water, but more difficultly soluble in benzene. We were unable to purify the base by recrystallization. A colorless, finely-crystalline substance of the composition $C_{13}H_{21}O_3N$, which softened at 38° and melted at 42-44°, $[\alpha]_D^{20}$ +34.52° (c 1.68, ethanol), was obtained by double distillation of the base at 100° and 0.2 mm. The base decolorized a sulfuric acid solution of $KMnO_4$ in the cold, and contained one hydroxyl group. According to the composition and properties of the resulting alkaloid, which was not described in the literature, we named it macrophylline.

In the literature there was mention concerning a base of composition $C_{13}H_{21}O_3N$, from Senecio sylvaticus and Senecio saracenicus [1], but no constants characterizing these alkaloids were cited.

On hydrolysis of macrophylline by 15% hydrochloric acid, it was decomposed to the amino glycol and angelic acid. The amino glycol was a crystalline substance with a m.p. of 126-128°, $[\alpha]_D^{20}$ +49.29° (c 1.60, ethanol), of composition $C_8H_{15}O_2N$, which formed a crystalline hydrochloride with a m.p of 152-153°, $[\alpha]_D^{20}$ +49.37° (c 1.37, ethanol), and decolorized an acid solution of $KMnO_4$ only on standing

The following amino glycols of composition $C_8H_{15}O_2N$ were described in the literature: platinesine [2, 3], with a m.p. of 151-152°, $[\alpha]_D^{20}$ −85°; dihydroxyheliotridan [4], with a m.p. of 76-77°, $[\alpha]_D$ −34°; khastanesine [5], with a m.p of 113-114°, $[\alpha]_D$ −9.07°, and turneforcine [6], with a m.p. of 118-120°, $[\alpha]_D$ −10.5°.

The "nesine" obtained from macrophilline was not described in the literature, and we named it "macronesine". Apparently, macronesine is a diastereoisomer of one of the described amino glycols of composition $C_8H_{15}O_2N$. On catalytic reduction of macrophilline with PtO_2, 1 mole of hydrogen was absorbed. Hydromacrophilline was a crystalline substance with a m.p. of 87-88° (petroleum ether), and a composition of $C_{13}H_{23}O_3N$. On hydrolysis of hydromacrophilline by 10% hydrochloric acid, "nesine" hydrochloride was obtained which gave no depression on determination of the melting point of a test sample of a mixture of macronesine hydrochloride obtained by hydrolysis of macrophilline. From the results of the analysis of the hydrolysis products and the catalytic reduction products of macrophilline, we can conclude that the new alkaloid is a monoester of macronesine and angelic acid. The unsaturated nature of macrophylline is explained by the presence of the double bond in angelic acid. The structure of macrophylline cannot be considered as definitely established.

EXPERIMENTAL

Isolation of the alkaloids. The dry, pulverized plant, in a quantity of 18 kg, was moistened with a small quantity of 10% ammonia, drained and extracted with dichloroethane. The dichloroethane solution was extracted with 10% H_2SO_4. The acid solution was filtered, cooled, alkalized with aqueous ammonia and extracted with ether, and then with chloroform. After removal of the ether, 10.93 g of a dark-cinnamon-colored, viscous substance was obtained. 14.5 g of a resinous substance was obtained, after removal of the chloroform.

Preparation of the tartrate salt. The total alkaloids obtained were dissolved in anhydrous alcohol, and an alcoholic solution of tartaric acid was added until the solution was acidic; the tartrate which precipitated was

separated and washed with alcohol. The weight of the tartrate from 10.93 g of total alkaloids was 2.16 g, its m.p. was 154-156°, and the weight of tartrate from 14.5 g of total alkaloids was 2.76 g, and its m.p. was 153-154°. After 3 recrystallizations of 4.92 g of the tartrate from alcohol, 2.5 g with a m.p. of 162-164° $[\alpha]_D$ +52.3° (l 0.5 dm, 0.0520 g in 4 ml of H_2O) was obtained.

4.160 mg sub.: 7.953 mg CO_2; 2.520 mg H_2O. 3.109 mg sub.: 6.008 mg CO_2; 1.920 mg H_2O. 9.512 mg sub.: 0.334 ml N_2 (21°, 724 mm) 9.402 mg sub.: 0.336 ml N_2 (20°, 726 mm). Found %: C 52.17, 52.73; H 6.78, 6.91; N 3.85, 3.83. $C_{17}H_{27}O_3N$. Calculated %: C 52.44; H 6.94; N 3.59.

Liberation of the base of macrophylline from the bitartrate. 1.1 g of the bitartrate was dissolved in 10 ml of H_2O, alkalized with 10% ammonia, and the alkaloid was extracted with ether. The ether solution was dried over Na_2SO_4, filtered and distilled, and the residue was 0.55 g of a crystalline, yellowish-colored substance. It was sublimed twice by heating on a boiling water bath (0.2 mm). During determination of the melting point, the substance softened at 38° and melted at 42-44°; $[\alpha]_D$ +34.52° (l 0.5 dm, 0.0058 g in 3.5 ml of anhydrous C_2H_5OH).

3.587 mg sub: 8.621 mg CO_2; 2.702 mg H_2O 4.666 mg sub.: 0.260 ml N_2 (21.5°, 723 mm). 9.661 mg sub: 0.520 ml N_2 (23.0°, 740 mm) 20.309 mg sub.: 2.04 ml CH_4 (20°, 761.0 mm). Found %: C 65.59; H 8.43; N 6.14, 6.06; OH 7.16. $C_{13}H_{21}O_3N$. Calculated %: C 65.27; H 8.78; N 5.85; OH 7.11.

Hydrolytic cleavage of the macrophylline with aqueous hydrochloric acid. 0.9 g of the base of macrophylline and 10 ml of 15% HCl were refluxed on a boiling water bath for 2 hours. The acid solution was extracted with ether. After removal of the ether 0.34 g of a crystalline acid, with a m.p. of 41-42°, which gave no m.p. depression with angelic acid, was obtained. The acidic aqueous solution was evaporated on the water bath. The weight of the macronesine hydrochloride was 0.7 g. Its weight was 0.55 g and its m.p. was 152-153° after 3 recrystallizations from anhydrous ethanol; $[\alpha]_D$ +49.37° (l 0.5 dm, 0.0482 g substance in 3.5 ml of C_2H_5OH).

4.097 mg sub.: 7.491 mg CO_2; 3.030 mg H_2O. 4.288 mg sub.: 7.881 mg CO_2; 3.128 mg H_2O. 14.420 mg sub: 0.917 ml N_2 (19.5°, 737 mm). 14.031 mg sub.: 0.921 ml N_2 (19.5°, 737 mm). 9.913 mg sub.: 5.12 ml 0.01 N $Hg(NO_3)_2$. 15.102 mg sub.: 7.78 ml 0.01 N $Hg(NO_3)_2$. Found %: C 49.90, 50.15; H 8.27, 8.16; N 7.20, 7.43; Cl 18.31, 18.27 $C_8H_{15}O_2N \cdot HCl$. Calculated %: C 49.61; H 8.26; N 7.23; Cl 18.39.

Liberation of the base of macronesine. 0.3 g of macronesine hydrochloride was dissolved in water, and 20% NaOH was added until the solution was alkaline to tropeolin O. The amino glycol was extracted with chloroform. The chloroform solution was dried over Na_2SO_4, filtered and distilled. The residue was recrystallized twice from acetone; its m.p. was 126-128°, $[\alpha]_D$ +49.29° (l 0.5 dm, 0.0568 g in 3.5 ml C_2H_5OH).

3.807 mg sub.: 8.550 mg CO_2; 3.248 mg H_2O. 3.788 mg sub.: 8.493 mg CO_2; 3.223 mg H_2O. 9.221 mg sub.: 0.720 ml N_2 (22.5°, 740 mm). Found %: C 61.29; 61.19; H 9.54, 9.52; N 8.61. $C_8H_{15}O_2N$. Calculated %: C 61.14; H 9.55; N 8.91

The amino glycol was readily soluble in water and in alcohol, but almost insoluble in ether.

Preparation of hydromacrophylline. Macrophylline (0.35 g) was dissolved in 20 ml of ethanol, 0.05 g of PtO_2 was added, and it was reduced with hydrogen at low pressure. 40 ml of hydrogen was absorbed. The catalyst was filtered off, and the alcohol was vacuum distilled. The weight of the reduced substance was 0.14 g (viscous oil). After treatment of the low-boiling fraction, crystalline hydromacrophylline was obtained, which after 2 crystallizations from petroleum ether melted at 87-88°; its weight was 0.07 g.

4.208 mg sub.: 10.017 mg CO_2; 3.672 mg H_2O. 5.102 mg sub.: 2.05 ml 0.01 N H_2SO_4 (by combination with NH_3). Found %: C 64.96; H 9.76; N 5.62. $C_{13}H_{23}O_3N$. Calculated %: C 64.73; H 9.54; N 5.80.

Hydrolytic cleavage of hydromacrophylline with aqueous hydrochloric acid. 0.05 g of hydromacrophylline, and 3 ml of 10% HCl were refluxed on a boiling water bath for 1 hour. The acid solution was extracted with ether. After removal of the ether 0.02 g of liquid acid was obtained, which we were unable to identify because of its insufficient quantity. The acidic aqueous solution was evaporated to dryness on the water bath, and the residue was recrystallized from anhydrous ethanol; its weight was 0.02 g, and its m.p. was 150-151°. In a mixture with macronesine hydrochloride the m.p. was 151-152°.

SUMMARY

1. A new alkaloid, macrophylline, of composition $C_{13}H_{21}O_3N$, was isolated from large-leaf ragweed (Senecio macrophyllus).

2. Angelic acid and an amino glycol of macronesine, of composition $C_5H_{15}O_2N$, not previously described, were formed by the acid hydrolysis of macrophylline.

3. Hydromacrophylline, of composition $C_{19}H_{23}O_3N$, was obtained by the catalytic reduction of macrophylline.

4. It was concluded that macrophylline is a monoester of macronesine and angelic acid.

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THE ALKALOIDS OF PANCRATIUM MARITIMUM

N. F. Proskurinina

The bulbs of Pancratium maritimum L. (see Amaryllidaceae), which were investigated, were collected July 25-26, 1953 on the shore of the Black Sea by the Caucasian expedition of the All-Union Scientific-Research Chemico-Pharmaceutical Institute, under the leadership of P. S. Massagetov. This plant had hardly been studied chemically until now [1].

The bulbs of Pancratium maritimum were extracted with dichloroethane, followed by extraction of the dichloroethane extracts with sulfuric acid. On alkalization of the acid extracts, a resinous precipitate of a mixture of bases was formed, from which two crystalline alkaloids were separated on the basis of their different solubilities in alcohol and in acetone.

One of the alkaloids, of composition $C_{18}H_{17}O_4N$ (I), with a m.p. of 260-262°, $[\alpha]_D$ −128.3°, was identified by direct comparison the lycorine [2].

The second alkaloid, of composition $C_{18}H_{21}O_5N$ (II), with a m.p. of 209-210° and $[\alpha]_D$+148.0°, was very close to narcissine in its properties and in the properties of its derivatives [3].

	Melting point	$[\alpha]_D$	Melting point of picrate	Melting point of methiodide	Neutral product of Hofmann decomposition (m.p.)
Narcissine	210-211°	+150.4°	205-208°	220°	101°
Base (II)	209-210	+148.0	204-205	218-219	107-109

After separation of a resinous precipitate [lycorine and base (II)], a base, with a m.p. of 184-186°, precipitated in crystalline form, which after crystallization from alcohol melted at 186-188°.

The alkaloid (III) thus obtained had the composition $C_{17}H_{19}O_5N$, was optically active ($[\alpha]_D$ −34.5°), and contained one methoxy, one hydroxyl and one methylenedioxy-group, on the basis of which its empirical formula could be represented as follows $C_{15}H_{12}(OH)(OCH_3)(CH_2O_2)ON$.

According to its properties, base (III) corresponded to neither one of the earlier known alkaloids. The name of pancratine was proposed for it. Pancratine was readily soluble in alcohol and in chloroform, more difficultly soluble in ether and in acetone, and almost insoluble in water. Pancratine gave crystalline salts with neither mineral nor organic acids. The crystalline methiodide, with a m.p. of 165-168°, was obtained by methylation of pancratine by methyl iodide in chloroform solution, without heating.

EXPERIMENTAL

Extraction of the alkaloids. Isolation of lycorine. 14 kg of dried, and finely crushed bulbs of Pancratium maritimum was mixed with 10% ammonia and extracted with dichloroethane, followed by extraction with 10% sulfuric acid. On alkalization of the sulfuric acid solution with ammonia, a resinous, reddish-cinnamon-colored precipitate came down, which was separated from the alkaline solution and mixed with alcohol. A grayish, powdery precipitate (4.8 g) with a m.p. of 223-225° was formed from the alcoholic solution. The resulting base was converted to the hydrobromide which, after 3 crystallizations from alcohol, had a m.p. of 211-212°. A test sample of a mixture of the resulting hydrobromide with lycorine hydrobromide gave no depression of the melting point.

The base was liberated from the hydrobromide by ammonia as a finely-crystalline, colorless precipitate. After washing with alcohol and recrystallization from alcohol, the base had a m.p. of 260-262°. A test sample of a mixture with lycorine gave no melting point depression.

0.0458 g sub.; 50 ml anhydrous alcohol, l = 2 dm, α_D −0.23°, $[\alpha]_D$ −125.6°.

Found %: C 66.72; H 5.77; N 4.68. $C_{18}H_{17}O_4N$. Calculated %: C 66.90; H 5.92; N 4.88.

Liberation of the base (II). After separation of lycorine the alcoholic mother liquor was vacuum distilled The residue, appearing as a dark, resinous substance, was treated with acetone; moreover, a yellowish, powdery precipitate (2.7 g) came down from the acetone, which after 3 crystallizations from acetone melted at 208-209°.

0.304 g sub.: 15 ml chloroform, l = 1 dm, α_D +3.0°, $[\alpha]_D$ +148.0°.

Found %: C 65.30, 65.29; H 6.24, 6.11; N 4.52, 4.52. $C_{16}H_{21}O_5N$. Calculated %: C 65.27; H 6.34; N 4.22.

The hydrobromide precipitated in crystalline form, on trituration of the base with aqueous hydrobromic acid. It melted at 202-203° after crystallization from alcohol.

0.1000 g sub.: 15 ml water, l = 1 dm, α_D +0.79°, $[\alpha]_D$ +118.

The hydrochloride came down as a finely-crystalline precipitate, on addition of alcoholic HCl to an alcoholic solution of the base The hydrochloride had a m.p. of 207-210° after crystallization from alcohol.

0.2000 g sub.: 15 ml water, l = 1 dm, α_D +1.54°, $[\alpha]_D$ +115.5°.

The methiodide: 2 g of the base, with a m.p. of 208-209°, was heated for 1 hour with 10 ml chloroform and 2 ml of methyl iodide. After removal of the solvent from the solution, a crystalline methiodide precipitate, with a m.p. of 218-219°, came down.

The Hofmann decomposition of the alkaloid (II) methiodide (narcissine) with moist silver oxide. 1st stage. 1 g of the alkaloid (II) methiodide in 25 ml of water was shaken with freshly-precipitated silver oxide until there was no reaction for halide in the aqueous solution. The precipitate was filtered off, the aqueous solution was evaporated to dryness in vacuo, and the residue was heated for 30 minutes on the water bath, and then extracted with ether. The des-base, as a light-yellow, oily substance, remained after removal of the ether. The crystalline hydrochloride, with a m.p. of 166-167°, precipitated on addition of alcoholic hydrochloric acid to the des-base.

The methiodide of the des-base of alkaloid (II). 1.2 g of the des-base of alkaloid (II) was dissolved in 12 ml of methyl alcohol, 1 ml of methyl iodide was added, and it was heated for 30 minutes. After removal of the solvent crystalline methiodide, with a m.p. of 171-173°, precipitated.

2nd stage. The methiodide of the des-base (0.5 g), with a m.p. of 171-173°, was shaken in 25 ml of water with moist silver oxide until there was no reaction for halide in the aqueous solution. The precipitate was filtered off and washed with ether. After removal of the ether, a crystalline precipitate with a m.p of 102-104° formed, which after crystallization from petroleum ether melted at 108-110°. The substance obtained was insoluble in water, and was also insoluble in acids and in alkalis.

Found %: C 73.55; H 5.16, $C_{14}H_{12}O_3$. Calculated %: C 73.68; H 5.16

Isolation of pancratine from the ether extract. After removal of the ether by which the alkaline solution was extracted, a yellowish, cystalline precipitate of the base (2.5 g), with a m.p. of 184-186°, formed. After crystallization from alcohol, the base (III) had a m.p. of 186-188°.

0.1000 g sub.: 15 ml chloroform, l = 1 dm, α_D −0.23°, $[\alpha]_D$ −34.5°.

Found %: C 64.54, 64.26; H 6.16, 6.02; N 4.42, 4.38; OH 6.33; OCH_3 9.51. $C_{17}H_{19}O_5N$. Calculated %: C 64.35; H 5.99; N 4.42; OH 5.3; OCH_3 9.81.

The methiodide. 0.75 g of the base with a m.p. of 186-188° was dissolved in 50 ml of chloroform, 2 ml of methyl iodide was added and it was allowed to stand for 24 hours. A crystalline precipitate with a m.p. of 162-164° came down from the solution; after washing it with alcohol its m.p. was 164-168°, and was unchanged after crystallization from alcohol.

SUMMARY

1. Three alkaloids were isolated from the bulbs of Pancratium maritimum: lycorine, narcissine and a new alkaloid of the composition $C_{17}H_{19}O_5N$, with a m.p. of 186-188° and $[\alpha]_D$ −34.5°, named pancratine.

2. Pancratine contains one hydroxyl, one methoxy and one methylenedioxy group. Its empirical formula is $C_{15}H_{13}(OH)(OCH_3)(CH_2O_2)OH$.

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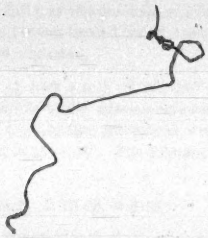

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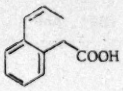
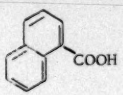
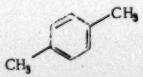
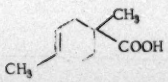
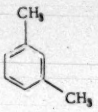
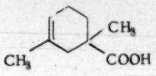
Page	Line	Reads	Should read
53	13 from bottom	l.mole^{-1} sec^{-1}	liter/mole^{-1} sec^{-1}
79	Formula, 2nd from top		
80	Formula	 (XXX)	 (XXX)
		 (XXIX)	 (XXIX)
146	Formula	$\xrightarrow[80\text{-}85^\circ]{Na_2SO_4}$	$\xrightarrow[80\text{-}85^\circ]{Na_2S_2O_4}$